THE STUDY OF MIXED VALENCE COMPOUNDS BY TIME DOMAIN REFLECTOMETRY

By

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Abstract of Dissertation Presented to the Graduate School of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

THE STUDY OF MIXED VALENCE COMPOUNDS BY TIME DOMAIN REFLECTOMETRY

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Sample termination Time Domain Reflectometry (TDR) is used to study the rates of electron transfer in solid mixed valence compounds. The frequency range used in this study was 5 MHz to 5 GHz. The temperature dependencies of the electron transfer mechanisms present in the compounds were studied.

This research benefited from improvements in the measurement equipment and in the equations used to analyze the time domain data. The data were analyzed in the frequency domain where the symmetrical response functions of the instrument could be cancelled and the errors created by electrical pulse propagation characteristics were corrected. A bilinear correction factor was applied to the frequency domain data to correct for recurring asymmetrical response functions of the equipment and undesirable transmission-line coupling reflections.

This project studied the symmetrical mixed valence compounds $[Fe_3(O)(CH_3OO)_6X_3] \cdot$ solvate, where (X is H_2O or C_5H_5N) and $[(bipy)_2Ru^{II}(BiBzIm)Ru^{III}(bipy)_2](PF_6)_5$, where bipy is 2,2'-

bipyridyl and BiBzIm is bibenzimidazolate. The rate of electron transfer of the latter compound was found to be outside the time scale of our equipment. The small changes in the real component of the dielectric constant as a function of frequency for the two former compounds created very small differences between the time domain responses of the sample and reference. These low-level signals provided poor signal-to-noise ratios and approached our ultimate detectivity limit.

The high frequency data of the imaginary component of the dielectric constant was greatly distorted in the iron trimer samples. This study proposes that this error resulted from the sample cell responding as a resistance, inductance, and capacitance circuit instead of as a simpler resistance and capacitance circuit. To correct these problems, several new sample cell designs were tried. Other equipmental changes are proposed based on initial testing of these designs.

This research did not provide a full characterization of the electron transfer mechanisms in these mixed-valence compounds. However, it has documented the effects of cell design and equipment artifacts. Future research must await additional improvements in the measuring apparatus and new theoretical treatments of the dielectric relaxation mechanisms in these mixed-valence compounds.

CHAPTER I
THEORETICAL BACKGROUND

Mixed Valence Compounds

Introduction

Mixed-valence compounds simultaneously contain atoms of the same element in different oxidation states.[1,2,3] These compounds may exhibit properties that are different from those of the individual sub-units comprising the complex or from the combined properties of the sub-units. These properties include a new electronic absorption, the intervalence transfer, a band resulting from electron transfer between the two metal centers which are in different oxidation states. If the complex has an intervalence transfer band, then it will also have a thermally-activated pathway for the same electron transfer process.[2,4,5] An energy of activation, E_a, is associated with the thermal process. The magnitude of E_a depends on (1) the ground-state potential-energy differences between the centers; (2) the degree of electronic and vibronic coupling between the centers; (3) the magnitude of the change in the bond lengths and the force constants that accompanies the change in the oxidation state of each metal center; and (4) the solvent reorganization or lattice-packing of ions, solvent molecules, or other mixed-valence compounds around the complex. Often the latter component may be the dominant factor affecting the rate of electron transfer.[2,3,6,7,8]

The compounds in this work are either $Ru^{II/III}$ or $Fe^{II/III}$ complexes bridged by the deprotonated 2,2'-bibenzimidazole or by the μ_3 - O and μ_2 - acetate groups, respectively. The electron transfer is likely to be exclusively via the bridges between the metal centers; thus, the intervalence electron transfer process is similar to an "inner sphere" electron transfer process. It is also similar to an "outer sphere" process since no bonds are broken.[1,3,8]

These and other mixed-valence compounds may be used as simplified models for precursor complexes of an intermolecular electron transfer reaction. This simplification can be demonstrated by use of a symmetrical mixed-valence dimer. This example assumes that the electronic coupling between the metal centers is small and under the constraints of Marcus theory. The free energy of activation, ΔG^*, for an outer sphere electron transfer reaction is[2,9,10,11]

$$\Delta G^* = \frac{W_r + W_p}{2} + \frac{\lambda_i + \lambda_o}{4} + \frac{\Delta G^o}{2} + \frac{(\Delta G^o + W_p - W_r)^2}{4(\lambda_1 + \lambda_o)}, \qquad \text{I-1}$$

where W_r and W_p correspond to the work to bring reactants together and to separate products, respectively; ΔG° represents the free energy difference between the reactants and the products; and λ_i and λ_o correspond to the inner and outer reorganizational energies of both metal centers during the reaction. The inner reorganizational energy is a function of the first three components affecting the magnitude of E_a, and λ_o is a function of the fourth

factor. In the case of electron transfer within the symmetrical mixed-valence compound used in this example, the reactant and product are the same molecule; therefore, W_r, W_p, and ΔG° are zero, leaving only λ_i and λ_o in the equation

$$\Delta G^* = \frac{\lambda_i + \lambda_o}{4} . \qquad \text{I-2}$$

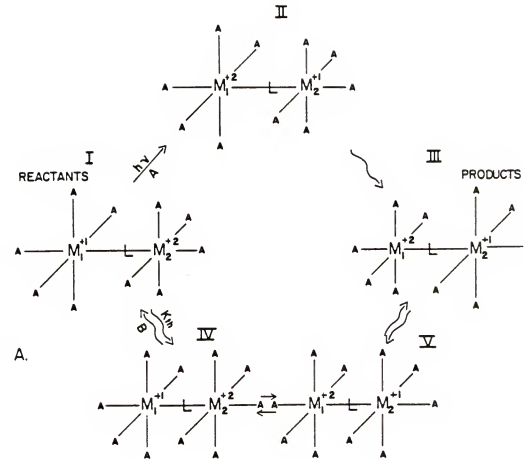
The origin of λ_i and λ_o in a symmetrical mixed-valence dimer, $(A)_5M_1^+ - L - M_2^{2+}(A)_5$, is illustrated in Figure I-1, where A refers to the ligands, and L refers to the bridge between the two metal centers. In Figure I-1A, the charges of M_1 and M_2 and the metal-ligand bond length changes are particularly significant. The complex is dissolved in a solvent and has a small electronic coupling, H_{AB} or ε (see below), between the sub-units.

The reactant is initially in the lower vibration energy level of the vibrational potential energy curve W_A in Figure I-1B. Compound I of Figure I-1A corresponds to this initial position of Figure I-1B. The metal-ligand bond lengths of the two sub-units become more alike as the complex moves "up" the potential energy curve toward the intersection of W_A and W_B. At the cross-over point, the intersection of W_A and W_B, all the bond lengths become identical. In pathway B of Figure I-1A, the equalizing of the M - A length for M_1 and M_2 depicts these bond length changes.

Each metal center, M_1 and M_2, has its own metal-ligand force constants, f_1 and f_2; equilibrium bond distances, d_1 and d_2, respectively; and solvent spheres.[3,7] The solvent sphere

Figure I-1. Bond length and vibrational potential-energy well changes that accompany the electron transfer in a symmetrical mixed-valence compound.

Part A depicts the bond length changes that accompany the electron transfer in the symmetrical mixed-valence compound, $(A)_5M_1^+ - L - M_2^{2+}(A)_5$, where L corresponds to the bridging ligand between the metal centers (i.e., M_1 and M_2), and A corresponds to the terminal ligand. Pathway A is for the optically-induced intervalence electron transfer, and pathway B is for the thermally activated electron transfer between M_1 and M_2. Part B shows the vibrational potential-energy wells for the electron transfer reaction demonstrated in Part A. The horizontal lines are the vibrational energy levels, with q corresponding to the vibration coordinates for the reactants and products. The vertical arrow demonstrates an optical transition of the reactant to an excited state of the products. The two molecules in the lower third of Part A, compounds IV and V, are at the cross-over point of the potential energy curves W_A and W_B in Part B.[3,7]


II
I
REACTANTS
III
PRODUCTS
IV
V
A.
B.
W_A
W_B
$q = -\lambda$
$q = \lambda$

surrounding the smaller +2-charged center will be different from the solvent sphere surrounding the larger +1-charged center. For the electron to be transfered by the thermal pathway B of Figure I-1A, the molecule must change its configuration so that the bond lengths are the same for M_1 and M_2; i.e., the molecule must be at the cross-over point of the W_A and W_B curves in Figure I-1B. As the bond lengths of each sub-unit change, the net charge and size of each sub-unit as seen by the solvent will also change. The solvent will therefore have to reorient around each sub-unit as the molecule approaches the cross-over point of W_A and W_B. The electron may then proceed "down" the W_B curve toward the products (compound III in Figure I-1A) or return to the reactants (compound I). The energy required to rearrange the bond lengths and solvent in order to reach the cross-over point of W_A and W_B constitutes an energy of activation. The rate constant for the thermal process is

$$k_{th} = K\upsilon_n \exp(-\Delta G^*_{th}/RT), \qquad \text{I-3}$$

where K corresponds to the adiabaticity factor, which equals one if the activated complex proceeds to product with unit probability, υ_n corresponds to the nuclear frequency factor (1 - 10) x 10^{12} sec^{-1} at 25 °C,[3] and ΔG^*_{th} corresponds to the energy of activation for the thermal process.[3,12]

The electron transfer may also proceed by an optical transition, the vertical arrow (Frank-Condon approximation) in Figure I-1B or pathway A in Figure I-1A. This electron transfer

process is an intervalence transfer transition in which the electron is excited from the W_A curve, reactant, to an excited state of W_B, product, at an energy of E_{op}.

In the terminology of the Piepho, Krausz, and Schatz (PKS) model, the bases of the parabolas (harmonic oscillator approximation) in Figure I-1B are displaced by 2λ, where λ is proportional to the average metal-ligand bond length change with oxidation state.[7,13] This implies that the two potential-energy curves are displaced further apart as the differences in their equilibrium metal-ligand bond distances, Δd, for each oxidation state of the metal become larger. This also implies that E_{op} will increased as λ or Δd become larger.

Classification of Mixed-Valence Complexes

For the sake of simplicity, the present discussion deals only with mixed-valence dimers. The mixed-valence dimer $(A)_5M_1^{+1}$ - L - $M_2^{+2}(A)_5$ has two sub-units, each of which has a corresponding wavefunction, Ψ_1 and Ψ_2, respectively, associated with it. Robin and Day,[14] devised a system which distinguishes three broad classes of mixed-valence compounds (see Figure I-2), Classes I, II, and III, which is often called the RD classification system. In this system Class I complexes have very little or no electronic coupling; i.e., H_{AB} equals approximately 0, where H_{AB} equals $< \Psi_1 \mid H_{el} \mid \Psi_2 >$ and H_{el} is the electronic coupling Hamiltonian operator that couples Ψ_1 and Ψ_2. In the limit of H_{AB} equal to 0, thermal and optical transfers are forbidden, and K equals 0,[15] (see

equation I-3). Class III complexes have large electronic coupling and have ΔG^{*}_{th} equal to 0. These compounds must be described by delocalized molecular orbitals. Class II complexes fall in between Class I and Class III complexes; they allow optical and thermal electron transfer, since H_{AB} is not equal to 0. In these complexes, the intensity of the intervalence absorption and the rate of thermal electron transfer increase as H_{AB} increases.

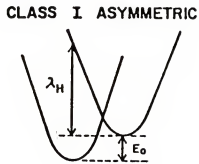
If the complex is asymmetric, one of the potential energy wells will be lowered by the amount E_o relative to the base of the other potential energy well. The energy of the optical transfer, $E_{op(H)}$, from the lower energy sub-unit to the higher energy sub-unit can be divided into two parts, i.e., $E_{op(H)}$ is equal to $E_o + \lambda_H$. The variable λ_H equals E_{op} for symmetrical complexes (see Figure I-2 and equation I-4b). The energy difference, E_o, will cause E_a for the forward and reverse electron transfer process to differ. In addition, the larger the E_o, the smaller the electronic coupling will be. These two factors tend to lock the valence of asymmetric complexes.

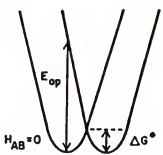
The two theories most often used to describe mixed-valence complexes are the Hush and the PKS Theories.

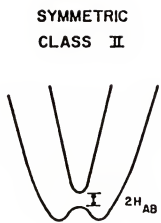
Hush Theory

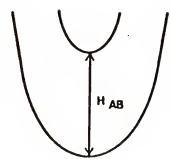
Hush theory is a high-temperature (semi-classical) limit model in which both λ_i and λ_o are treated.[3,4,7,13,16,17] The solvent is considered a dielectric continuum.

Figure I-2. Potential energy wells for the Robin and Day classification of symmetric and asymmetric mixed-valence compounds. As electronic coupling increases, the gap between the upper and lower surfaces increases, and the energy of activation for the thermal electron transfer decreases.


CLASS I ASYMMETRIC
λ_H
E_o


CLASS I
E_{op}
$H_{AB}=0$
ΔG^*


SYMMETRIC
CLASS II
$2H_{AB}$


CLASS III
H_{AB}

The assumptions made in this theory are (reference 13, page 156)

1. Weak electronic coupling.
2. Harmonic potential energy surfaces.
3. Identical normal mode frequencies in both potential energy surfaces.
4. Strong vibrational-electronic interactions.
5. Vibrational intervals [i.e., the energy gap between vibrational energy levels] which are much smaller than kT.

The basic Hush equations are

$$\Delta G^{*}_{th} = E_{op}/4, \qquad \text{I-4a}$$

$$\Delta G^{*}_{th} = \frac{(\lambda_H + E_o)^2}{4\lambda_H}, \qquad \text{I-4b}$$

$$\Delta \bar{\nu}_{1/2} = [(16 \ln 2kT)\ \bar{\nu}_{max}]^{1/2} (cm^{-1}), \qquad \text{I-5a}$$

$$\Delta \bar{\nu}_{1/2} = \sqrt{2312\ \bar{\nu}_{max}}, \quad \text{at Room Temperature,} \qquad \text{I-5b}$$

$$\Delta \bar{\nu}_{1/2} = \sqrt{\bar{\nu}_{max} - 2312\ E_o}, \quad \text{at Room Temperature} \qquad \text{I-5c}$$

$$\alpha^2 = H_{AB}{}^2 = \frac{4.24 \times 10^{-4}\ \epsilon_{max} \Delta \bar{\nu}_{1/2}}{\bar{\nu}_{max}\ R^2}, \qquad \text{I-6}$$

$$E_{op} = E_{inner} + E_{outer}, \qquad \text{I-7}$$

$$E_{inner} = n\left(\frac{2\ f_1 f_2}{f_1 + f_2}\right)(d^0_1 - d^0_2)^2, \qquad \text{I-8}$$

$$E_{outer} = e^2 \left[\frac{1}{2a_A} + \frac{1}{2a_B} - \frac{1}{R}\right]\left[\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_s}\right] , \qquad \text{I-9}$$

where E_{op}, E_o, ΔG^*_{th}, f_1, f_2, d_1, and d_2 have been previously defined, e equals the charge of the electron, a_A, a_B are equal to metal-ligand bond lengths for each sub-unit of the dimer, ε_{max} equals the maximum molar absorptivity ($M^{-1}cm^{-1}$), R(Å) equals the separation of the two metal centers, and ε_∞ and ε_s are the optical and static dielectric constant. The optical dielectric constant is often taken as the refractive index of the solvent. The band at half-width, $\Delta\bar{\nu}_{1/2}$, is defined as the $\Delta\bar{\nu}$ when the following criterion is met:

$$\frac{I_{\bar{\upsilon}}\,(\bar{\upsilon}_{max})}{I_{max}\,(\bar{\upsilon})} = 1/2 \qquad \text{I-10}$$

Various versions of Equation I-9 have been tried with varying degrees of success; Creutz has reviewed several of these variations.[3]

As stated above, the Hush theory is for weakly coupled complexes (the Frank-Condon approximation applies), and the fundamental metal-ligand vibrational frequency, ν_-, is assumed to be much less than kT ($\nu_- \ll kT$). When these restrictions are not satisfied, the theory is no longer valid. As H_{AB} and the electron transfer rate, k_{th}, are increased, the assumption that ν_- is much less than kT becomes less acceptable. It has been suggested that ν_- is approximately equal to kT for the heavier metals, e.g., ν_- for the Ru - NH_3 bond; thus, the "high-temperature limit"

assumption by Hush may not be valid for many mixed-valence complexes which contain the heavier metals.[2]

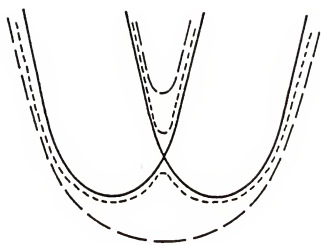
The electronic wavefunctions for the states of the mixed-valence complex before and after electron transfer are defined $\Psi_{M_1^+M_2^o}$ and $\Psi_{M_1^oM_2^+}$, respectively. Electronic coupling mixes these two states to produce new upper and lower states[7,12,13] (see Figure I-3). If H_{AB} is moderate and k_{th} is slow on the vibrational time scale, then the splitting of the two curves equals $2H_{AB}$ as in Figure I-2, the Class II complex. However, if k_{th} becomes fast on the vibrational timescale (i.e., as the Born-Oppenheimer approximation fails), the splitting between the potential energy surfaces changes with q (see Figure I-1B for q); i.e., as the intersection region (cross-over point) is approached, the two states mix more.[12] A model is necessary to account for mixed-valence compounds which do not fit the "high-temperature limit" assumption of Hush theory.

PKS Theory

The PKS theory is a vibronic coupling model which ignores all solvent effects and bridging ligand effects.[6,7,8,13] The solution to the dynamic case partially accounts for the sample not adhering to the assumption that ν_- is much less than kT. The assumptions for the theory are

1. The harmonic approximation for the potential energy wells is used in the "static" model; i.e., the Born-Oppenheimer approximation is valid. (See Figure I-1B for an example of the

Figure I-3. Potential energy wells to demonstrate the effect of increased electronic coupling.[13] Initially, when H_{AB} equals 0, there are two overlapping potential energy wells. In this situation, the electron cannot transfer from one potential energy well to the other. As electronic coupling increases, new higher and lower energy states are produced from mixing the two initially non-interacting states Φ_1 and Φ_2 (see RD classification above). As H_{AB} becomes large, the molecules become a RD Class III compound.



——— H_{AB} = 0

------ H_{AB} = INTERMEDIATE VALUE

— — H_{AB} = LARGE VALUE

wells.)

2. Only the totally symmetric normal coordinates of each center, Q_A and Q_B, participate in the electron transfer process. Only one totally symmetric normal coordinate is assumed for each center.

3. The force constants for the metal-ligand bond are the same for both centers, thereby removing any cross terms, $Q_A \times Q_B$, in the potential energy equations for states ψ_a and ψ_b. The terms ψ_a and ψ_b are analogous to the previously mentioned $\Psi_{M_1^+M_2^0}$ and $\Psi_{M_1^0M_2^+}$, respectively (see equations I-14 and I-15).

4. In the dynamic or non-adiabatic case, ψ_a and ψ_b are allowed to be at most slowly varying functions of q (see Figure I-1B).

The static model is described below. The theory assumes that the mixed-valence complex is A^NB^M, where A and B are the sub-units and N and M are the oxidation states of the metal centers. The reaction of interest is $A^NB^M \dashrightarrow A^MB^N$, where the electron has been transferred between the two metal centers (see Figure I-1). Both sub-units are assumed to follow a parabolic potential energy surface, e.g., the potential energy surface W_M^A for the sub-unit A^M is

$$W_M^A = W_M^0 + 1_M^A Q_A + 1/2\, k_M^A Q_A^2, \qquad \text{I-11}$$

where Q_A equals the totally symmetric normal coordinate of A, i.e., for the symmetric stretch for the complete sub-unit, and k_M^A equals

the metal-ligand force constant for A^M. There are analogous equations for W_N^A, W_M^B, and W_N^B. The potential energy curves of the sub-units are combined to produce harmonic potential energy wells for the complete mixed-valence complex, W_a and W_b, with the corresponding electronic wavefunctions, ψ_a and ψ_b, respectively. Assuming that 1. N is the more stable (i.e., lower in energy) oxidation state, 2. that Q_A and Q_B are equal to zero at the base of their respective potential energy wells, and 3. that

$$l_M^A = l_M^B \equiv l,\ k_M^A = k_M^B \equiv k_M, \text{ and } k_N^A = k_N^B \equiv k_N\ ,$$

where l is proportional to the difference of d_1 and d_2, and is defined by equation I-11, then the equation for the potential energy of each state of the complex is

$$W_a = W_N^A + W_M^B = lQ_A + \tfrac{1}{2} k_M Q_A^2 + \tfrac{1}{2} k_N Q_B^2, \qquad \text{I-12}$$

$$W_b = W_M^A + W_N^B = lQ_B + \tfrac{1}{2} k_M Q_B^2 + \tfrac{1}{2} k_N Q_A^2. \qquad \text{I-13}$$

If we introduce new coordinates $Q_\pm$, which equals $(1/\sqrt{2})$ $(Q_A \pm Q_B)$, and assume that k_M, k_N and k are equal, then the potential energy equations become

$$W_a = (1/\sqrt{2})\, lQ_- + \tfrac{1}{2} kQ_-^2 + (1/\sqrt{2}) lQ_+ + \tfrac{1}{2} kQ_+^2\ , \qquad \text{I-14}$$

$$W_b = (-1/\sqrt{2})\, lQ_- + \tfrac{1}{2} kQ_-^2 + (1/\sqrt{2}) lQ_+ + \tfrac{1}{2} kQ_+^2\ . \qquad \text{I-15}$$

The latter assumption implies that the two sub-units have identical force constants for the metal-ligand bonds. The potential energy equations are now separable into Q_+ or Q_- terms. The former yields two overlapping curves and does not affect the properties connected with the intervalence transfer. If the assumption that k_M equals k_N is valid, then the Q_- term yields two non-overlapping potential curves, and Q_+ can be neglected in the following equations.

If the fundamental vibration frequency associated with Q_- is ν_-, which equals $(2\pi)^{-1}\sqrt{k}$ and the new variables

$$q = 2\pi[\nu_-/h]^{1/2} Q_-; \quad \lambda = 1[8\pi^2 h(\nu_-)^3]^{-1/2}, \qquad \text{I-16}$$

are introduced, then

$$W_a/h\nu_- = \lambda q + 1/2\, q^2; \quad W_b/h\nu_- = -\lambda q + 1/2\, q^2 . \qquad \text{I-17}$$

Figure 1-1B illustrates these two potential energy curves by changing W_a for W_A and W_b for W_B. In this equation, the two minima are separated by 2λ, and λ is proportional to the difference between d_1 and d_2. The significance of q is also demonstrated in Figure I-1A. When q equals $-\lambda$, the structure of the complex appears as the structure I in Figure I-1A, while at q equal to $+\lambda$, the corresponding structure is III; i.e., the bond lengths of structure I are reversed to produce III. Either structure IV or V corresponds to q equals 0. One can now allow vibronic (vibrational-electronic coupling) and electronic coupling between

the sub-units while the molecule maintains the Born-Oppenheimer approximation. The vibronic coupling is a function of λ; i.e., the larger λ is, the faster the two potential energy wells will rise in energy as a function of q, and the further apart the minima of the potential energy wells will be. Also when an optical intervalence transition occurs, vibrational excitation of the mixed-valence molecule will be higher (see Figure I-1B). The degree of vibronic coupling therefore increases as λ increases. The sub-units are electronically coupled by the electronic coupling Hamiltonian operator V^{AB}. The electronic coupling parameter is defined as

$$\varepsilon = V^{\circ}_{01} /(h\nu_{-}), \qquad \text{I-18}$$

where V°_{01} is equal to $< \psi_a|V^{AB}|\psi_b >$, and V^{AB} couples ψ_a and ψ_b at their equilibrium positions to yield new upper and lower energy molecular waveforms, ψ_2 and ψ_1, respectively.

By application of first order perturbation theory, one may obtain the secular determinant to solve for the new potential energy curves; W_k, where k equals 1 or 2, in energy units of $h\nu_{-}$ is

$$\begin{vmatrix} W_a - W_k & \varepsilon \\ \varepsilon & W_b - W_k \end{vmatrix} = 0 \quad ,$$

which equals upon substitution for W_a and W_b

$$\begin{vmatrix} \lambda_q + 1/2\, q^2 - W_k & \varepsilon \\ \varepsilon & -\lambda_q + 1/2\, q^2 - W_k \end{vmatrix} = 0 .$$

The roots are

$$W_{1,2} = q^2/2 \mp (\varepsilon^2 + \lambda^2 q^2)^{1/2}, \qquad \text{I-19}$$

and the resulting electronic wavefunctions are obtained from the solution of ψ_k equals $C_a\psi_a + C_b\psi_b$, where k equals 1 or 2, when

$$\sum_{k\,=\,1,2} \sum_{\substack{i\,=\,a,b \\ j\,=\,a,b}} C_j(H_{ij} - S_{ij}W_k) = 0. \qquad \text{I-20}$$

In this equation, H_{ij} equals $\langle \psi_i \mid V^{AB} \mid \psi_j \rangle$, and S_{ij} equals $\langle \psi_i | \psi_j \rangle$, which equals 0 if i is not equal to j. The results are

$$\psi_{1,2} = \mp \frac{1}{N\sqrt{2}} [\pm(\varepsilon \pm \lambda q - \sqrt{\varepsilon^2 + \lambda^2 q^2})\, \psi_a \ \ldots \qquad \text{I-21}$$
$$+ (\varepsilon \pm \lambda q - \sqrt{\varepsilon^2 + \lambda^2 q^2})\, \psi_b] ,$$

with $N = [\, \lambda^2 q^2 + (\varepsilon - \sqrt{\varepsilon^2 + \lambda^2 q^2}\,)^2]^{1/2}$. The energies of $\psi_{1,2}$ are functions of q and λ. The latter parameter is ignored by the Hush theory. The energy of activation is also a function of ε and λ.

$$\frac{\Delta G^*_{th}}{h\nu_-} = \frac{1}{2}\lambda^2 - |\varepsilon| + \frac{\varepsilon^2}{2\lambda^2} \quad \text{when } |\varepsilon| \leq \lambda^2 \qquad \text{I-22}$$

These equations for $\psi_{1,2}$ and ΔG^*_{th} give insight into factors affecting electron transfer. The most important items are that

1. The wave functions, $\psi_{1,2}$, are sensitive functions of q.

2. The electronic coupling parameter, ε, mixes ψ_a with ψ_b and ε is proportional to the mixing of ψ_a with ψ_b.

3. The greater the energy difference of the zero order curves $|W_a - W_b|$, the less mixing of ψ_a and ψ_b; $|\frac{1}{W_a - W_b}|$ is proportional to the mixing of ψ_a with ψ_b.

4. Vibronic coupling (which is a function of λ and is a parameter that is ignored by most theories) has a significant contribution to intervalence electron transfer processes. As an example, if the bond lengths A^N - Ligand and A^M - Ligand, are significantly different, then the complex may become a "trapped" class I complex, even if the complex is symmetrical.

The extension of the static to the dynamic case is beyond the scope of this dissertation. The PKS model gives better insight into the inner shell factors affecting the electron transfer rates of mixed-valence compounds than do RD or Hush models.

However, the theory does have problems. It assumes that ε is small compared to the electronic binding energies within the sub-units, i.e., that it ignores any mixing of the ground state wavefunctions of the sub-units with their excited states. Also, it completely ignores any mixing of the bridge and metal orbitals, as well as any contribution of asymmetric vibrations of the complex. It is likely as electronic coupling increases that the latter two effects become more important and the model, consequently, less

valid. In addition, the theory ignores spin-orbital coupling effects. Finally, as mentioned above, the theory covers only inner shell effects. The factors listed above have been shown to have significant effects on the calculated values produced by the PKS model and, therefore, on the rates of electron transfer. The theory does, however, explicitly indicate that the vibrations of the mixed-valence molecule may have significant effects on the intervalence electron transfer rate.[6,7,9,18,19]

Dielectric Relaxation

Introduction

An ideal dielectric material has no conductivity; i.e., it is a perfect insulator.[1,2] Real insulating materials, however, are not perfect. Their electrons clouds and ions may become polarized when the insulator is placed in an electric field. If a real dielectric material is placed in a parallel-plate capacitor and an external field, E_0, is applied, the material will become polarized to oppose the field. In this section, a bold face symbol implies that the variable is a vector. The induced field is E_1. The net field, E_2, across the capacitor is

$$E_2 = E_0 + E_1. \qquad \text{I-23}$$

The dielectric constant of the material is

$$\varepsilon = E_0/E_2. \qquad \text{I-24}$$

Switching the polarity of the parallel plates will induce the dipoles of the dielectric sample to switch directions. At some frequency, f, of switching the polarities of the plates, the dipoles of the material will lag behind the applied field, and E_1 will decrease. From equation I-24 it is seen that, if E_1 becomes smaller, so must ε. This movement of the dipoles in response to the applied electric field is called dielectric relaxation, the phenomena of which will first be analyzed in a static-field case, then expanded to include dynamic fields.

Static Fields

The response of dielectric material to an applied field is most easily understood in a constant field parallel plate capacitor.[20,21] The area of the plates must be large compared to the gap, d, between the plates in order to minimize edge effects. (See Figure I-4a for a diagram of the capacitor.) The plates have a charge of $\pm$ Q per unit area before the sample is added. The electric field between the plates, E, in a vacumm is

$$E = V/d, \qquad \text{I-25}$$

where V equals the voltage applied to the plates. This electric field is directly proportional to Q,

$$Q = \varepsilon_0 E, \qquad \text{I-26}$$

Figure I-4. Parallel plate capacitor.

Part a. Parallel plate capacitor with a vacuum between the plates. The plates obtain a charge of ± Q and are separated by a distance of d.

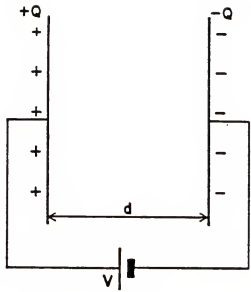
Part b. The dielectric sample between the plates is polarized to produce charges ± P on its surface.

E_0 = Externally applied electric field driven by voltage V.

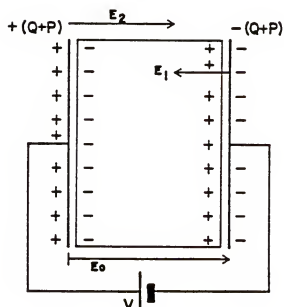
E_1 = The induced electric field of the dielectric material.

E_2 = The net electric field (which equals the vectorial addition of E_0 to E_1) across the capacitor.

$$E_2 = E_0 + E_1$$



(a)



(b)

where ε_0 is the permittivity of free space ($\varepsilon_0 = 8.85 \times 10^{-12}$ Fm^{-1}). The vacuum capacitance per unit area is

$$C_0 = Q/V. \qquad \text{I-27}$$

If the capacitor is filled with a non-polar isotropic material, then the material will become polarized with charges, ± P, on its surface (see Figure I-4b). In the figure, the total number of charges on the plates is greater than with a vacuum between the plates. The vector quantities $\mathbf{E_0}$, $\mathbf{E_1}$, and $\mathbf{E_2}$ mentioned in the introduction to this section are also drawn in Figure I-4b. The sample-filled cell stores more energy than the vacuum cell since, the cells have a capacitance, C, of (Q + P)/V and Q/V, respectively. The ratio of C to C_0 is the static dielectric constant of the material

$$\varepsilon_S = C/C_0 = \frac{Q + P}{Q} = \frac{\varepsilon_0 \vec{E} + \vec{P}}{\varepsilon_0 \vec{E}}, \qquad \text{I-28}$$

where $\vec{E}$ and $\vec{P}$ are equal to **E** and **P**, respectively, and **P** is the vectorial representation of the net polarization of the material in the capacitor.

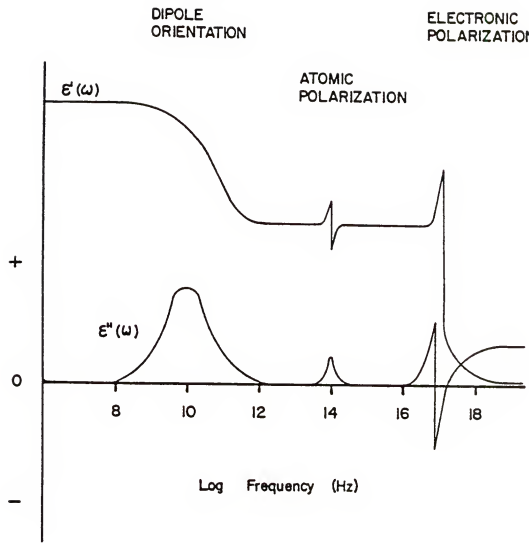
On a molecular level, the polarization results from three frequency-dependent mechanisms. These mechanisms, in decreasing order of excitation frequency, are electronic, atomic, and orientational polarization. Electronic polarization is the induced displacement of the electrons relative to the nuclei. Atomic

polarization is the induced movement of the nuclei in a molecule or lattice. Normally, the effect of atomic polarization is approximately one-tenth that of electronic polarization; yet, in some ionic lattices, e.g., NaCl, the relative shifting of all positive ions in relation to all negative ions can produce significant contributions.[20] Orientational polarization is found in molecules with permanent dipoles. These initially random permanent dipoles attempt to align themselves parallel to the applied field, while thermal motion tends to randomize them. As the sample temperature is decreased, the total induced polarization, P, of polar molecules will increase more rapidly and be of larger magnitude than for non-polar molecules, because the effect of thermal motion on the molecules aligning with the field will be less.[21] Figure I-5 shows the frequency dependence of the three types of molecular polarization and that dipole orientation is the slowest (lowest frequency) of the three types of polarization. There are two curves drawn, one for $\varepsilon'(\omega)$ and the other for $\varepsilon''(\omega)$; a detailed description of these will be given below. The value of $\varepsilon'(\omega)$ at the low frequency end equals ε_s. Also, the rapidly changing portion of $\varepsilon'(\omega)$, which is located over log (frequency) equals 14, corresponds to the index of refraction of the material.

In addition, since polar molecules have all three forms of polarization, they will generally display larger P and ε_s. Equation I-28 can be rearranged to solve for P as a function of E

$$P = (\varepsilon_s - 1)\varepsilon_0 E. \qquad \text{I-29}$$

Figure I-5. The frequency dependence of the three types of molecular polarization.[20,22]



$\varepsilon'(\omega)$ = FREQUENCY DEPENDENT DIELECTRIC CONSTANT

$\varepsilon''(\omega)$ = LOSS FACTOR

The quantity $\varepsilon_o\varepsilon_s E$ is the electrical displacement, D, of the material

$$D = \varepsilon_s\varepsilon_o E = \varepsilon_o E + P. \qquad \text{I-30}$$

Equations I-29 and I-30 are general equations for the static and time variant fields if the frequency dependent dielectric constant $\varepsilon(\omega)$ replaces ε_s.[22]

On the time scale of the instruments that measure changes in orientation of dipoles, the electronic and atomic polarizations are fast. These two forms of polarization, therefore, appear instantaneous in the experiment. Also, unlike electronic or vibrational transitions, in which the molecule makes quantized jumps from a lower to a higher energy level, a resonance phenomenon, the molecular dipole reorientation consists of thermally-dampened adjustments of their average orientation, a "relaxation phenomena."

Time Variant Fields

The discussion below assumes that the dielectric material is a linear dielectric which obeys the superposition principle,[20,21,22] i.e.,

$$E(t) = E(t = 0) + \sum E(t_i), \qquad \text{I-31}$$

$$P(t) = P(t = 0) + \sum P(t_i), \qquad \text{I-32}$$

where t_i equals the time when a change in P(t) or E(t) occurs, and P(t) and E(t) are now the time dependent electric field and polarization.

Before discussing the effect of the time dependent E(t) on the macroscopic polarization, it is instructive to look at the pre-equilibrium time-dependent dipolar relaxation of a sample in a constant-potential parallel-plate capacitor. In the long time limit, the sample will obtain a new equilibrium position for its net dipole moment. The time dependent electric field vector, E(t), yields a frequency dependent polarization and a frequency dependent dielectric constant. The frequency dependent polarization and pre-equilibrium polarization are mathematically connected by the Fourier or Laplace Transforms.

When voltage is applied to a sample filled capacitor, there is an "instantaneous polarization," P_1, i.e., electronic and atomic polarization, of the sample, followed by the reorienting of the dipoles in response to the applied field to their final position. The instantaneous polarization yields the high frequency dielectric constant, ε_∞. The static dielectric constant, ε_s, is obtained when the dipoles reach their new equilibrium position and the polarization of the material has reached its new maximum value, P_f.

Let $P_2(t)$ equals the departure of the polarization from its equilibrium value,[21] and assume that the rate at which $P_2(t)$ approaches P_f follows Einstein's diffusion theory[19] prediction, i.e., that $dP_2(t)/dt$ is proportional to the departure of the total polarization from its equilibrium value.[21] Then

$$\frac{dP_2(t)}{dt} = \frac{P_f - P_1 - P_2(t)}{\tau}, \qquad \text{I-33}$$

where τ equals the macroscopic time constant for the reorientation. It is now possible to solve equation I-33 for $P_2(t)$ using the boundary conditions that

$$E(t) = 0 \text{ at } t < 0, \text{ and } E(t) = V_0 \text{ at } t \geq 0,$$

where V_0 equals the final value of E(t), and then

$$P_2(t) = (P_f - P_1)\,[1 - \exp(-t/\tau)]. \qquad \text{I-34}$$

From equation I-34 it is seen that the total macroscopic polarization of the sample and, therefore, the time dependent dielectric constant, $\varepsilon(t)$, are both exponentially increasing functions (see equations I-35 - I-36 and Figure I-6 for a graph of these functions).

$$P(t) = P_1 + (P_f - P_1)\,[1 - \exp(-t/\tau)], \qquad \text{I-35}$$

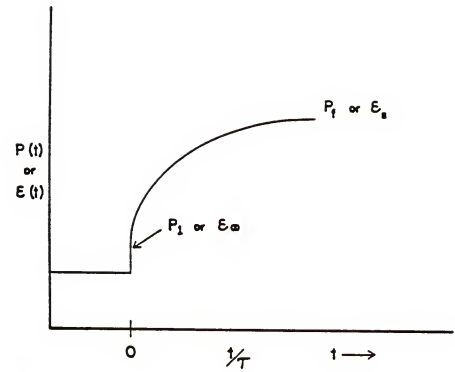
and

$$\varepsilon(t) = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty)\,[1 - \exp(-t/\tau)], \qquad \text{I-36a}$$

or

$$\varepsilon(t) = \varepsilon_s + (\varepsilon_\infty - \varepsilon_s)(\exp(-t/\tau)). \qquad \text{I-36b}$$

Figure I-6. Plots the real part of the time-dependent polarization and dielectric constant of a polar sample. The time-dependent polarization and dielectric constant instantaneously jump to the values of P_1 or ε_∞ when the electric field is first applied. The two functions then exponentially approach their final values of P_f or ε_s.



$$\overrightarrow{P(t)} = \overrightarrow{P_i} + (\overrightarrow{P} - \overrightarrow{P_i}) \left[1 - \exp.(t/\gamma)\right]$$

$$\varepsilon(t) = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty)(1 - \exp.(-t/\gamma)) = \varepsilon_s + (\varepsilon_\infty - \varepsilon_s)(\exp.(-t/\gamma)$$

One can apply to the sample an alternating electric field, $E(t)$, which equals $E_0 \exp(i\omega t)$, with a time dependent voltage $V(t)$, which equals $V_0 \exp(i\omega t)$, whose real components are[20,22]

$$E(t) = E_0 \cos[\omega t], \qquad \text{I-37}$$

$$V(t) = V_0 \cos[\omega t]. \qquad \text{I-38}$$

In this equation, E_0 and V_0 are the amplitudes of the electric field and the voltage vectors, respectively, and ω equals $2\pi f$ which is the angular frequency. As ω is increased, the polarization will at some frequency start to lag behind the applied field. This lag of the polarization vector causes the dielectric displacement, $D(t)$, to be out of phase with $E(t)$ by a frequency dependent phase angle, $\delta(\omega)$,

$$D(t) = D_0 \cos[\omega t - \delta(\omega)], \qquad \text{I-39a}$$

$$D(t) = D_1(\omega) \cos[\omega t] + D_2(\omega) \sin[\omega t], \qquad \text{I-39b}$$

where D_0 equals the amplitude of the sinusoidal variation, and

$$D_1(\omega) = D_0 \cos[\delta(\omega)],$$

$$D_2(\omega) = D_0 \sin[\delta(\omega)].$$

Equation I-39 can be rewritten using a different notation

$$\mathbf{D}(t) = \varepsilon'(\omega)\ \mathbf{E_0}\cos[\omega t] + \varepsilon''(\omega)\ \mathbf{E_0}\sin[\omega t], \qquad \text{I-40}$$

where $\varepsilon'(\omega) = \dfrac{\mathbf{D_1}(\omega)}{\varepsilon_0\ \mathbf{E_0}}$, $\quad \varepsilon''(\omega) = \dfrac{\mathbf{D_2}(\omega)}{\varepsilon_0\ \mathbf{E_0}}$,

and

$$\tan\delta(\omega) = \varepsilon''(\omega)/\varepsilon'(\omega). \qquad \text{I-41}$$

The first term of equation I-40 is the "in phase" component of **D**(t) with respect to E(t). It contains the frequency dependent dielectric constant, $\varepsilon'(\omega)$, which reduces to ε_s at low frequencies. The loss factor, $\varepsilon''(\omega)$, is a measure of the amplitude of the "out of phase" by 90° component of **D**(t). This factor is a measure of the energy loss in the form of heat as the dipoles attempt to follow E(t).

The two terms $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ may be combined to give the complex dielectric constant

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\ \varepsilon''(\omega). \qquad \text{I-42}$$

The real component is the dispersion mode, while the imaginary component is the energy absorption mode of the material interacting with E(t).

The charging current of the capacitor, i.e., the sample cell in Time Domain Reflectometry (see Chapter I, Section: Time Domain

Reflectometry) is also a function of $\varepsilon^*(\omega)$. If the voltage, $V(t)$, which equals $V_0 e^{i\omega t}$, is applied, then the charging current $I(t)$ is

$$I(t) = \varepsilon^*(\omega)\, C_0 \frac{dV(t)}{dt}, \qquad \text{I-43}$$

$$I(t) = i\omega[\varepsilon'(\omega) + i\varepsilon''(\omega)]C_0 V, \qquad \text{I-44}$$

$$I(t) = \omega C_0 \varepsilon''(\omega)V(t) + i\omega C_0 \varepsilon'(\omega)V(t), \qquad \text{I-45}$$

$$I(t) = I_R + I_C, \qquad \text{I-46}$$

where I_C and I_R are the capacitive component (leading the potential by 90°) and the resistive component (in phase with the potential) of the charging current of the capacitor, respectively, and all other symbols have previously been defined.

The resistive component (which contains $\varepsilon''(\omega)$) can do work, i.e., give off heat, while the capacitive component (which contains $\varepsilon'(\omega)$) can store the energy.

For a Debye Dielectric material, $\varepsilon^*(\omega)$ can be represented as[20,21,22]

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_\infty}{1 + i\omega\tau}, \qquad \text{I-47a}$$

where $\varepsilon'(\omega) = \varepsilon_\infty + \dfrac{\varepsilon_S - \varepsilon_\infty}{1 + (\omega\tau)^2}$ and, I-47b

$$\varepsilon''(\omega) = \frac{(\varepsilon_S - \varepsilon_\infty)\omega\tau}{1 + (\omega\tau)^2}. \qquad \text{I-47c}$$

(See Figure I-7 for graphs of these functions.)

Figure I-7 and equation I-47c show that the maximum energy absorption is when $\omega\tau$ equals 1. The macroscopic relaxation time constant, τ, can thus be derived from the inflection point of $\varepsilon'(\omega)$ or the peak maximum of $\varepsilon''(\omega)$ versus $\log(\omega)$.

As seen in Figure I-7, real data are often broader than the Debye theory predicts, and it is often difficulty to determine τ accurately from these broadened curves. Tau can be determined more accurately by the linearization of equations I-47b-c.[21] (See equations I-48 - I-53, for convenience, ε'' equals $\varepsilon''(\omega)$, ε' equals $\varepsilon'(\omega)$, ε^* equals $\varepsilon^*(\omega)$, and x equals $\omega\tau$.)

$$x = \varepsilon''/(\varepsilon' - \varepsilon_\infty) \qquad \text{I-48}$$

$$x = (\varepsilon_S - \varepsilon')/\varepsilon'' \qquad \text{I-49}$$

$$x/\varepsilon'' = x^2/(\varepsilon_S - \varepsilon_\infty) + 1/(\varepsilon_S - \varepsilon_\infty) \qquad \text{I-50}$$

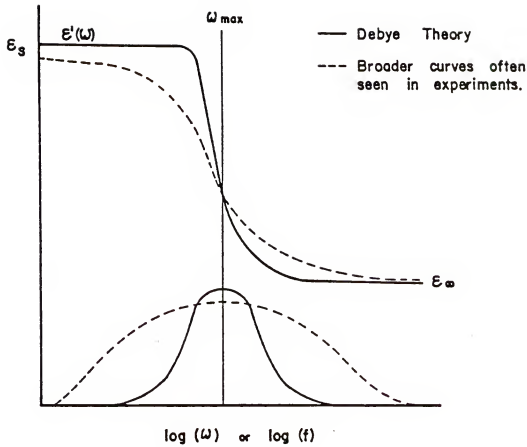
$$1/\varepsilon''x = 1/(\varepsilon_S - \varepsilon_\infty)x^2 + 1/(\varepsilon_S - \varepsilon_\infty) \qquad \text{I-51}$$

$$1/(\varepsilon' - \varepsilon_\infty) = x^2/(\varepsilon_S - \varepsilon_\infty) + 1/(\varepsilon_S - \varepsilon_\infty) \qquad \text{I-52}$$

$$1/(\varepsilon_S - \varepsilon') = 1/(\varepsilon_S - \varepsilon_\infty)x^2 + 1/(\varepsilon_S - \varepsilon_\infty). \qquad \text{I-53}$$

Only equations I-48 or I-49 are considered in this dissertation. These two equations lead to four graphical systems to obtain τ. They are graphing ε''/ω vs. ε', ε''/f vs. ε', $\varepsilon''\omega$ vs. ε', or $\varepsilon''f$ vs.

Figure I-7. The solid line shows the idealized dispersion, $\varepsilon'(\omega)$, and the energy absorption, $\varepsilon''(\omega)$, modes as a function of log (frequency) for a Debye dielectric material, following equations I-47b and c. The dotted line depicts the shape of the same functions broadened by experimental factors and multiple relaxations.[20,22]


ω_{max}
$\varepsilon'(\omega)$
ε_s
Debye Theory
Brooder curves often seen in experiments.
ε_∞
log (ω) or log (f)

ε', where ω and f are the angular frequency and frequency, respectively, to obtain τ or f_c for the process, where f_c equals $1/(2\ \pi\tau)$.

Dispersion versus absorption, DISPA, plots are useful to indicate how well the relaxation process fits a Debye dielectric type relaxation, how many types of relaxation processes are present, and to discern τ.[20,21,22,23,24] The Debye semicircle, which is a form of DISPA, is derived by rearranging equation I-48 and I-49 to give

$$(\varepsilon' - \frac{\varepsilon_s - \varepsilon_\infty}{2})^2 + (\varepsilon'')^2 = (\frac{\varepsilon_s - \varepsilon_\infty}{2})^2 . \qquad \text{I-54}$$

(See Figure I-8 for the Cole-Cole plot based on a system having only one Debye relaxation.)

If the dielectric material has a distribution of relaxation times, each of which gives rise to a Debye type behavior, then their DISPA are better described by the Cole-Cole arc, equation I-55, or by the Cole-Davidson arc, equation I-56.

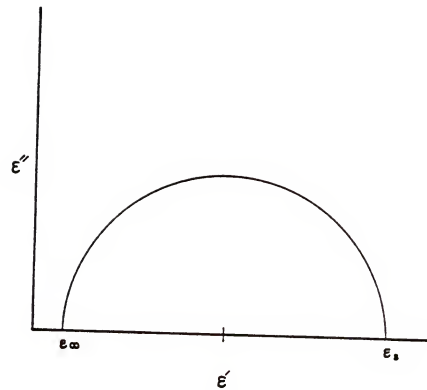
$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau)^\alpha} \qquad \text{I-55}$$

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{(1 + i\omega\tau)^\beta} \qquad \text{I-56}$$

If the total relaxation process is described by the summation of Debye type relaxation processes, then ε^* can also be described by

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_1}{1 + i\omega\tau_1} + \frac{\varepsilon_2 - \varepsilon_3}{1 + i\omega\tau_2} + \ldots, \qquad \text{I-57}$$

Figure I-8. Cole-Cole Plot or a Debye Semicircle. The semicircle intercepts the x-axis at the values of ε_s and ε_∞.


ε''
ε∞
ε'
εs

where the numerator is the $\varepsilon_s - \varepsilon_\infty$ of each relaxation process.

In all these situations of frequency dependent dielectric relaxation, ε' refers to a real component of the dielectric constant which decreases in magnitude with increasing frequency; and ε'' is a measure of the energy absorbed from the applied electric field. It is dissipated by the "friction" created by the dipoles attempting to follow the field. The macroscopic time constant, τ, yields the critical frequency, f_c, which is the applied frequency at which the induced movement of the dipole moment of the sample is the same as the frequency of the voltage, E(t), being applied to the capacitor.

Until recently, ε', ε'', and τ were collected by frequency-by-frequency fixed frequency domain analysis.[3,19,20,21,25,26,27,28] This process is slow and expensive and often yields incomplete dispersion data. As shown earlier, the time dependent polarization, P(t), (equation I-35 and I-36) is connected with the frequency domain analysis parameters. All the information obtained from the frequency domain analysis can be acquired by following the time dependent charging of a dielectric filled capacitor. The time domain data are Fourier transformed to give the frequency domain data more rapidly. This process is called Time Domain Reflectometry (TDR) or Time Domain Spectroscopy (TDS).[29]

The electron transfer rate of mixed-valence compounds can be obtained by TDR if the electron transfer rate is slowed down enough by an appropriate energy of activation to the time scale of TDR.[3,19,30,31,32] The electron movement produces a dipole moment shift, i.e., dielectric relaxation. Measuring electron movement by

dielectric relaxation methods has been done with mixed-valence compounds,[3,19,30] polymers, and biological complexes.[33,34,35,36]

Time Domain Reflectometry

Introduction

Sample termination TDR as it is considered in this work has a frequency range of (10 - 100) KHz to 10 GHz.[37] It measures dielectric absorption by coupling all electric dipoles to the externally applied field. This relaxation process may be the result of (1) electron transfer between site isolated centers, (2) dc conductivity, (3) librations, (4) diffusion, (5) interfacial polarization, (6) lattice vibrations, (7) and thermal expansion/contraction of the lattice.[38] The complex dielectric constant, ε^*, and τ or f_c are obtained by comparison of the time dependent charging currents of an air filled cell (capacitor) with a sample filled cell.

The TDR apparatus is schematically drawn in Figure I-9A.[4,39,40,41,42]

Figure I-9B demonstrates the total voltage, V(t), on the oscilloscope. All voltage reflections from the sample cell are totaled at the oscilloscope and are added to the incident voltage pulse to produce V(t). In Figure I-9A the magnitude of the reflected voltages decreases with time, e.g., R1, R2.... A voltage pulse generator (tunnel diode) produces an approximate square wave, $V_o(t)$, with a rise time, Tr, less than 25 psec and length of approximately 500 nsec. The voltage pulse passes through the Sampler (Tr < 30 psec) point A, where the voltage pulse is detected

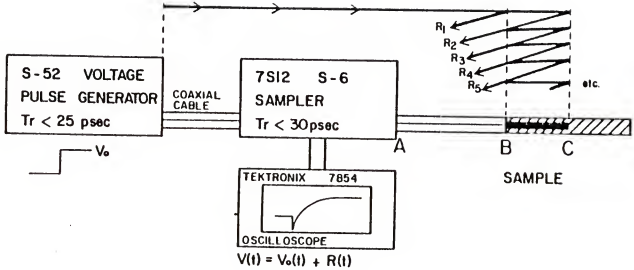
Figure I-9. Block diagram of the TDR equipment and the total voltage reflections from the sample cell.

Part A. Block diagram of the TDR equipment and the reflections from the sample. The voltage pulse from the S - 52 voltage pulse generator reflects off the two interfaces at positions B and C and are summed at the sampler, position A.

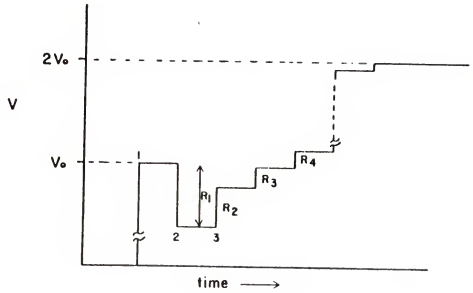
Part B. The total voltage at the oscilloscope is the result of the summation of the incident step pulse, $V_0(t)$, and the reflections from the sample cell, R1, R2, ... The final voltage value, $2V_0$, is twice the magnitude of the incident pulse voltage. The voltage train consists of three parts:

1. $V_0(t)$ passes position A;
2. First reflection from sample surface, position B, passes position A; and
3. Reflections from within the sample pass position A.

A.


S-52 VOLTAGE
PULSE GENERATOR
Tr < 25 psec
COAXIAL CABLE
7S12 S-6
SAMPLER
Tr < 30psec
Vo
A
B
C
SAMPLE
R1
R2
R3
R4
R5
etc.
TEKTRONIX 7854
OSCILLOSCOPE
V(t) = Vo(t) + R(t)

B.


2Vo
V
Vo
R1
R2
R3
R4
1
2
3
time

and displayed on the oscilloscope. The pulse continues down the next section of coaxial line until it encounters the sample, point B in Figure I-9. The impedance of the coaxial cable, which normally has a characteristic impedance of 50 ohms, and the sample are different. Part of the pulse is thus reflected, R1, from this interface back toward point A again, while the rest of the pulse continues to point C. As R1 passes the sampler, its voltage is added to the voltage of the incident pulse and is displayed on the oscilloscope (see Figure I-9). At point C, virtually all of the pulse is reflected back toward B, where part of the signal is transmitted toward A and the rest is reflected back again to C. The second reflection, R2, arrives at the sampler 2d/c later than R1, where the distance between B and C is "d", and "c" is the speed of propagation through the sample. (The speed of propagation through the sample cell and the coaxial cable connected to it is normally assumed to equal the speed of light.) Ideally, this process will continue until all of $V_o(t)$ is reflected back past A. The first reflection has a negative reflection coefficient (see equation I-60) and is out of phase with $V_o(t)$. The rest of the reflections are from the transmission of the reflected pulses through the interface at B and are in phase with $V_o(t)$ (see Figure I-9B). All the voltage reflections are superimposed at the oscilloscope, i.e., the total voltage at point B or anywhere else in the coaxial line between the sample and sampler at any time $t > 0$ is thus the summation of $V_o(t) + R(t)$, where $R(t)$ is the total voltage resulting from the reflections.

If the sample has no dc conductance, then the reflected pulse

will rise to a voltage of $2V_o$. If air is the sample, all of $V_o(t)$ will be reflected back in phase from the end of the center post, point C. The image on the oscilloscope screen will therefore rise rapidly from V_o to $2V_o$. Ideally, this rise comes from one reflection. In this work, the experimentally derived risetime for the air sample is approximately 50 psec. Figure I-10 shows the oscilloscope trace of methanol and air. Figure I-11 shows the oscilloscope trace of n-propanol and air. The more polar methanol sample in Figure I-10 has a larger initial dip, resulting from the first reflection, R1.

General Theory and Equations

As stated above, the reflections are the result of impedance mismatches.[38,42,43,44] Impedance, Z, of a non-conducting sample in a coaxial line with characteristic impedance, Z_o, is

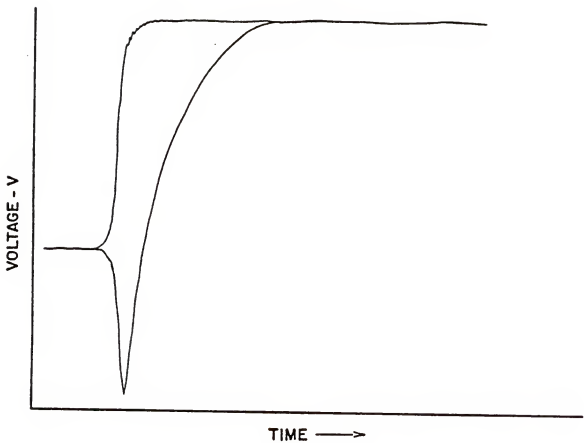
$$Z = \frac{Z_o}{\sqrt{\varepsilon^*}}, \qquad \text{I-58}$$

and for a conducting sample,

$$Z = \frac{i\omega L + R}{\sqrt{i\omega\varepsilon^* C + G}}, \qquad \text{I-59}$$

where L is the inductance, R equals the series resistance, and G equals the parallel conductance. This equation can be rewritten using conductivity, σ, instead of G, where σ equals the conductivity in siemens/cm ($G/4c\pi$). The reflection coefficient, ρ, is

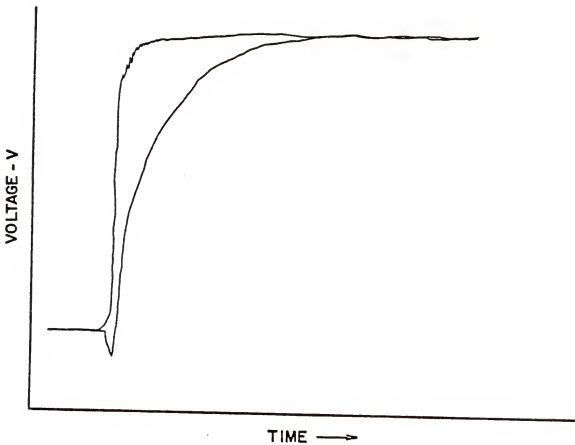
Figure I-10. The oscilloscope trace for CH_3OH (lower figure) and air. The ripples seen at the top of the air spectra are the result of unwanted reflections.



CH_3OH

5 NSEC. WINDOW

Figure I-11. The oscilloscope trace for n-propanol (lower figure) and air. The initial dip resulting from the first reflection (at point B in Figure I-9A) of propanol is smaller than that of the more polar methanol sample in Figure I-10.



n - PROPANOL

5 NSEC. WINDOW

$$\rho = \frac{1 - \sqrt{\varepsilon^*}}{1 + \sqrt{\varepsilon^*}} . \qquad \text{I-60}$$

For a sample other than air, $\sqrt{\varepsilon^*}$ is greater than 1; thus, Z is less than Z_0 and, as mentioned above, the first reflection from the sample has a negative reflection coefficient (see equations I-58 and I-59).

Unwanted impedance mismatches within the TDR circuitry may cause problems. An especially troublesome situation occurs when a voltage signal is propagated through a coaxial line which has both of its connectors of lower impedance than Z_0 of the cable.[45] The voltage signal then bounces back and forth between the two ends. If this happens to be the cable connected to the sample cell, part of the bouncing pulse will be transmitted into the sample and "re-excite" the sample. This process is repeated many times. The spectrum on the oscilloscope is, therefore, a combination of many overlapping reflections from the sample and from any other impedance mismatches of the system. The obvious correction for this problem is to match all impedances as best as possible, but it is impossible to remove all mismatches. This problem can be corrected however, by calibrating the instrument by use of a bilinear correction factor (see below).

The equation for deriving ε^* from sample termination TDR, which shall be called TDR from here on, is derived by analyzing the input admittance of the sample cell. The voltage pulse $V_0(t)$ is initially assumed to be a $\delta(t)$ function which rises instantly to a value of V_0 at t equals 0.

The charging of a capacitor which has the geometric capacitance of C_g, is filled with a dielectric sample, and, if under the influence of $V_o(t)$, will produce the corresponding charge of $Q(t)$[20,29,40,46,47,48]

$$Q(t) = C_g[\varepsilon_\infty V_o(t) + \int_{-\infty}^{t} V_o(t')\dot{\Phi}(t - t')dt'] , \qquad \text{I-61}$$

and

$$\phi(i\omega) = L\Phi(t) = \int_0^\infty \Phi(t) \exp(-i\omega t)dt , \qquad \text{I-62}$$

$$\varepsilon^* = L[\dot{\Phi}(t)] + \varepsilon_\infty = i\omega\phi(i\omega) + \varepsilon_\infty . \qquad \text{I-63}$$

In this equation, Φ (t) equals the macroscopic dielectric relaxation function,[49,50] $L[\Phi(t)]$ is the Laplace transform of $\Phi(t)$, and $\phi(i\omega)$ is the complex frequency dependent dielectric response function. The term $\varepsilon_\infty V_o(t)$ in equation I-61 is extracted from $\Phi(t)$ to emphasize that there is an instantaneous component combined with the slower component. These are the same instantaneous and slower components that were previously discussed in the development of the time dependent polarization, P(t), and the dielectric constant, $\varepsilon(t)$, in Chapter I, Section: Dielectric Relaxation (see equations I-34 - I-36 and Figure I-6). In the following sections, $\varepsilon_\infty V_o(t)$ is contained within $\Phi(t)$. The charging current and sample admittance, $y(i\omega)$, are

$$i(i\omega) = L[\partial Q(t)/\partial t] = C_g\, i\omega\varepsilon^*\, v(i\omega) , \qquad \text{I-64}$$

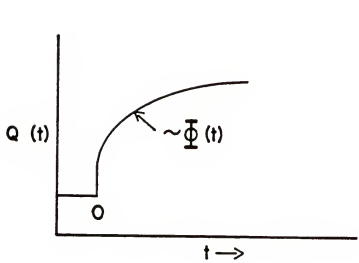
$$y(i\omega) = i(i\omega)/v(i\omega) = i\omega\varepsilon^{*}C_{g} \quad , \qquad \text{I-65}$$

where $v(i\omega)$ equals $L[V(t)]$. The idealized charging current and charge of the capacitor are shown in Figure I-12 and I-13. Figure I-13 shows the complete square wave, V(t); the charging and discharging of the capacitor are thus shown in the figure. Figure I-13, parts c and d, also shows the conduction present which consumes part of the energy of the electric field, E(t), to drive the electrons through the sample.

The sum of the reflections from the sample resemble the idealized I(t) curves in Figure I-12 and I-13. However, these reflections are distorted by instrumental and wave propagation effects and therefore do not perfectly coincide with the idealized I(t) curves. The factors distorting the reflections are given below.

1. The incident pulse, $V_0(t)$, has a finite risetime, Tr, instead of being a $\delta(t)$ function.
2. The amplitude of the reflected pulse is modified by the cables, connectors, etc.
3. It is assumed that the pulse travels at the speed of light, c, through both the cable and sample. Yet the pulse travels slower than c, since the pulse is modified by the sample and the sample cell. This leads to a delay greater than the assumed 2d/c, where d equals the sample depth, between reflected pulses, e.g. R1, R2, ... (see Figure I-9).

Figure I-12. Transient charge, Q(t), and current, I(t), of a polar dielectric sample following an ideal step pulse.[47,48] Their connection to the macroscopic dielectric relaxation function is given in equations I-61 and I-64.


Q (t)
~Φ (t)
0
t →

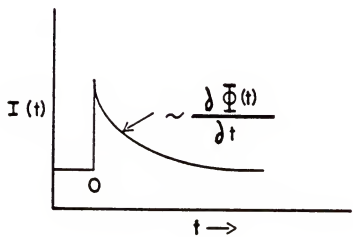
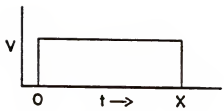

I (t)
~ ∂Φ(t)/∂t
0
t →

Figure I-13. The charging and discharging of a capacitor as a function of time.

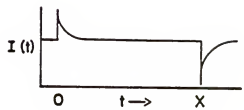
This figure shows the charging and discharging of the capacitor as a function of time. This is in contrast to the previous figure which showed only the charging of the capacitor. The value of X in this work is approximately 500 nsec.

The figure demonstrates the transient voltage, V, and current, I(t), across a capacitor when the idealized step voltage or square wave potential shown is (a) is applied across (b) a dielectric with dipolar relaxation, (c) a conductor, and (d) a dielectric with conductance and dipolar relaxation.[20]

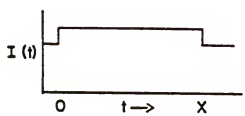
Sample (d) is conducting and therefore its current does not return to the baseline as I(t) did with the nonconducting sample (a).



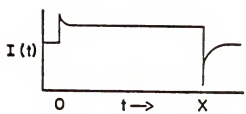
(a)



(b)



(c)



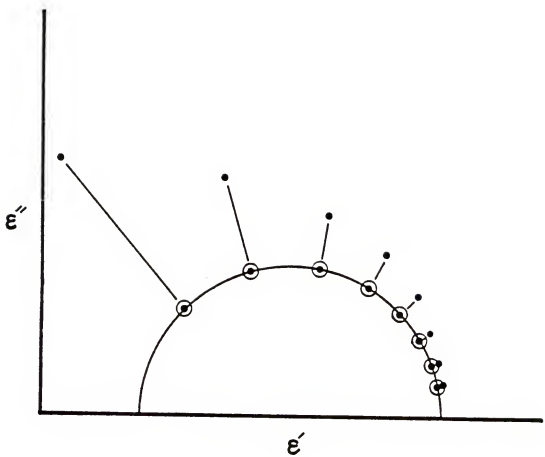
(d)

4. The base line voltage on the oscilloscope, instead of being a constant value, has a slowly rising and falling signal superimposed on it.
5. The electronics of the oscilloscope causes ringing before and after rapid current or voltage changes.
6. The response time of the TDR equipment is finite.

These six distortions of V(t), which are detected at the sampler, change the short time and the high frequency behavior of the real sample. The previous work by Kroeger[2,31,32] and Bunker,[1] where the data was acquired and analyzed in the time domain, only partially corrected these distortions.[41,51,52] All of these problems, except the fourth, can be explicitly accounted for in the equations for ε^* derived from input admittance analysis, which include corrections for propagation effects. Figure I-14 demonstrates the errors caused by one not accounting for propagation effects. Significantly, the error becomes larger at the higher frequencies. Improvements in the electronics of the digitizing oscilloscope have reduced the problem resulting from the fourth item listed above.

In the derivation of the input admittance analysis equations, it will initially be assumed possible to obtain an ideal open circuit, i.e., that there are no fringing fields or stray capacitance in the sample cell.[29,46,47,52] The voltage, V(t), at the front face of the sample, point B in Figure I-9, is $V_o(t)$ + R(t), where $V_o(t)$ is the non-ideal incident voltage pulse and R(t) is the voltage resulting from the reflections at the sample. The

Figure I-14. This figure illustrates the effect of correcting for propagation in the sample. The points on the semi-circle are corrected by use of f(Z) (equation I-71), while the non-corrected points show an increasing deviation from the correct values as the frequency increases. The points above the semi-circle are at the same frequency as the point they are connected to on the semi-circle.[51]


ε″
ε′

input current, I(t), of the sample cell is $G_c[V_o(t) - R(t)]$, where G_c equals $(L_c/C_g)^{1/2}$ and is the characteristic conductance of a loss-free coaxial line with geometric capacitance, C_g, and inductance, L_c, per unit length. The complex input admittance of the sample cell, $y_{in}(i\omega)$, equals

$$y_{in}(i\omega) = \frac{L[I(t)]}{L[V(t)]} = G_c \frac{[v_o(i\omega) - r(i\omega)]}{[v_o(i\omega) + r(i\omega)]} , \qquad \text{I-66}$$

$$y_{in} = G_c \frac{(v_o - r)}{(v_o + r)} = G_c \frac{p}{q} , \qquad \text{I-67}$$

where p equals $L(V_o(t) - R(t))$, which also equals $L(V_o(t)) - L(R(t))$; q equals $L(V_o(t) + R(t))$; and L equals the Laplace transform. The analogous time domain functions P(t) and Q(t) are defined as $V_o(t) - R(t)$ and $V_o(t) + R(t)$, respectively. They correspond to their respective frequency-dependent analogs, p and q. In equation I-67, the $(i\omega)$ term was dropped for convenience. The ratio of $i(i\omega)/v(i\omega)$ of the complex input admittance at the sample cell (equations I-66 - I-67) is the same as that received by the sampler during the experiment.

If the sample cell is regarded as a symmetrical four terminal network, then y_{in} is given by

$$y_{in} = \frac{y_o + y_d}{1 + Z_s y_d} , \qquad \text{I-68}$$

where y_o equals the open circuit admittance which equals $i\omega C_g d\varepsilon^*/f(Z)$, y_d equals the input admittance terminating the sample cell, and Z_s equals the short circuit impedance. This equation is

derived from network theory which is beyond the scope of this work.

To rephrase equation I-68 in terms of this experiment, y_d is be the load, e.g., a 50 Ω resistor, connected to the end of the sample cell center pin. The open circuit admittance is the admittance when there is no electrical connection between the electrodes, e.g., y_d equals 0.

For sample termination TDR, y_d equals 0 and equation I-68 becomes

$$y_{in} = y_o = \frac{i\omega C_g \varepsilon^* d}{f(Z)} . \qquad \text{I-69}$$

This equation is similar to equation I-65 except that now the sample has a finite depth and the pulse propagation through the sample is accounted for by the factor f(Z).

Combining equations I-69 and I-67 gives the following rearrangement when c is substituted for $\frac{G_c}{C_g}$

$$\varepsilon^* = c/d \frac{\rho}{i\omega q} f(Z) , \qquad \text{I-70}$$

where c equals the speed of propagation (which is assumed to equal the speed of light); d is the sample depth; f(Z) equals Z cot Z; and Z is $(\omega d/c) \sqrt{\varepsilon^*}$. A power series approximation of f(Z) yields

$$f(Z) = 1 - 1/3 \ (\omega d/c)^2 \varepsilon^* - \frac{1}{45}(\omega d/c)^4 \varepsilon^{*2} + ... \qquad \text{I-71}$$

The propagation correction factor, f(Z), converges to zero for

Z less than $\pi/2$, but the recommended limit is for Z to be less than 1. This latter limit is recommended to minimize possible errors in the f(Z) approximation as it approaches a value of zero. This lessens the frequency range for samples with large ε^*, i.e., those in which the maximum frequency is given by $\omega < c/(d\sqrt{\varepsilon^*})$. Cole, in his most recent papers,[46,53] uses a modified series expansion for f(Z)

$$f(Z) = 1 - A(\omega d/c)^2\varepsilon^* \qquad \text{I-72}$$

where A is approximately equal to 1/3, and is an empirical constant derived from calibration with known standards.

In either of these systems, ε^* is first approximated by setting f(Z) equal to 1, i.e., by making it the first term of the series expansion. The value of ε^* obtained when f(Z) equals 1 is then substituted into the following term of the series to calculate the next level of approximation of ε^*.[52] This iterative procedure works because the f(Z) series rapidly converges for most ω being studied.

Equations I-70 - I-72 need two modifications. First, in the actual experiment, the reference is air, (see below) which has ε' approximately equal to 1, and ε'' approximately equal to 0. The measured complex dielectric constant must, therefore, be modified to account for the reference. Secondly, the cell is not an ideal circuit, i.e., there is radiation into the external medium and/or the cell has an effective y_d characterizing its stray capacitance. The second situation is corrected by calibrating the

sample cell with known standards at low frequencies for an effective electrical depth, d, which is greater than the actual depth. The final equation, after the correction for the ε^* of air is added in, is

$$\varepsilon^* - 1 = [(c/d)\ p/i\omega q][1 - A(\omega d/c)^2(\varepsilon^* + 1) + \ldots], \quad \text{I-73}$$

where A equals 1/3.

A subtlety that one may miss in the above discussion is that $V_o(t)$ (which equals $(L^{-1}v_o)$) is actually produced when the incident pulse passes point A in Figure I-9.[37,53,54] The incident pulse can be closely approximated by use of an "open circuit" sample cell with an effective electrical depth, d, and an appropriate reference. The values of the dielectric constant of the reference, ε_R, must be known and real. Also the propagation correction factor, f(Z), for the reference must equal 1 over the frequency range to be studied. The obvious choice is air, which has an ε_s equal to 1. The reflection(s) from the air-filled sample cell comes from the end of the center pin, point C in Figure I-9, while the reflections from the sample filled cell are from point B; i.e., there is a total forward and reverse time of flight difference of 2d/c. If $R_R(t)$ is the reflection(s) from the reference, then

$$v_o = [L[R_R(t)]]\ \exp(i\omega 2d\varepsilon_R/c), \quad \text{I-74}$$

or

$$V_o(t) = R_R[t + 2d\epsilon_R/c] \ , \qquad \text{I-75}$$

where $L[R_R(t)]$ is phase shifted by $2\omega d\epsilon_R/c$ (equation I-74) or the reflection is shifted to earlier time by $2d\epsilon_R/c$ (equation I-75).

In this work, $R_R(t)$ is shifted in the frequency domain by using a modification of Cole's "Two-Position [Difference] Method" equation.[54,55]

The two-position method uses a two-position sample cell to cancel out v_o; i.e., the time domain data for each sample are acquired twice. The data are first acquired in the normal manner. The cell has its usual effective electrical depth, d_o. The experiment is repeated with a new center electrode, which has an effective electrical depth, d. The new center electrode is a metal rod, which has a larger outer diameter than the original center electrode and is notched at its base so that it can fit over the original center electrode of the cell.

If the reference is air, then f(Z) is approximately equal to f_o, which equals $1 - 1/3(\omega d_o/c)^2$ where d_o is the effective electrical depth used with the reference cell. In the single-position cell, d_o equals d since the cell has only one center electrode. Using equation I-70, ϵ^* is

$$\epsilon^* = \frac{c}{d_o i\omega} \frac{v_o - r_o}{v_o - r_o} f_o \ , \qquad \text{I-76}$$

where r_o is the reflection from air when air is being used as the sample, while v_o is the reflection from air as the reference. The time shift of $2d_o/c$ (the time delay between the reference and the

sample reflections) can be reformulated in the frequency domain by rearranging equation I-76; thus,

$$\frac{v_o - r_o}{v_o + r_o} = \frac{i\omega do}{cf_o} \quad , \qquad \text{I-77}$$

and then solving equation I-77 for v_o

$$v_o = r_o \frac{[1 + \frac{i\omega d_o}{cf_o}]}{[1 - \frac{i\omega d_o}{cf_o}]} \quad . \qquad \text{I-78}$$

The second cell position of the "Two-Position Cell" equivalence of equation I-70 is

$$\varepsilon^* = \frac{c}{\gamma d i\omega} \frac{(v_o - r)}{(v_o + r)} f(Z) \quad , \qquad \text{I-79}$$

where γd is the effective electrical length of the sample cell. A substitution of equation I-78 into equation I-79 cancels out v_o. Using the conditions of γ equals 1 and d equals d_o for a single position cell yields equation I-80

$$\varepsilon^* - \varepsilon^*_{Ref} = \frac{[1 - 1/3(\frac{\omega d}{c})^2 \varepsilon^*_{app}]}{1 - (\frac{\omega d}{c})^2(\frac{1}{3} + \varepsilon^*_{app})} f(Z) \quad , \qquad \text{I-80}$$

where ε^*_{app} equals $\frac{c}{di\omega} \frac{Diff(\omega)}{Sum(\omega)}$, $Diff(\omega)$ equals the difference of the reference and sample waveforms, and $Sum(\omega)$ equals the summation of the same waveforms. Equation I-80 is the working equation for our system. It is similar to one that Kroeger

suggested that the group try.[56] His equation is

$$\varepsilon^* - \varepsilon^*_{Ref} = \frac{(1 - (\omega d/c)^2 \varepsilon^*_{Ref})(\varepsilon^*_{app})}{1 - (\omega d/c)^2 \varepsilon^*_{app}(\varepsilon^*_{Ref})} \; f(Z) \; , \qquad \text{I-81}$$

where f(Z) equals $1 - A(\omega d/c)^2(\varepsilon^* + \varepsilon^*_{Ref})$, and A is approximately equal to 1/3. If a time shift not obtainable with equation I-80 is required, then equation I-82 is used

$$\varepsilon^* - \varepsilon_{Ref} = \frac{[\varepsilon_{23}] + \frac{c}{\omega d} \tan \frac{\omega \delta t}{2}}{1 - \frac{\omega d}{c} \tan(\frac{\omega \delta t}{2})[\varepsilon_{23}]} \; f(Z) \; , \qquad \text{I-82}$$

where ε_{23} equals the right hand side of equation I-80 without the f(Z) correction.

Time Domain Transformations

The time domain data is converted to the frequency domain by the Discrete Fourier Transform, DFT,

$$f(\omega) \doteq \Delta \sum_{n=1}^{N} f(n\Delta) \exp(-i\omega n\Delta) \; , \qquad \text{I-83}$$

where Δ is the time interval between each time domain point and $n\Delta$ is the time of each of these points.[29,47,48,52,55] To obtain each frequency data point, $f(\omega)$, the term $\exp(-i\omega n\Delta)$ is multiplied by every time domain point. In the program KDSAM9E.FOR, the exponential is converted into the sine and cosine form to improve the speed and accuracy of the computation.

The DFT equation (see equation I-83) works well for waveforms that have the same initial and final values. It can be used for the Diff(ω) data when dc conductivity is negligible (see below). Because the initial and final values for Sum(ω) are vastly different, sizeable leakage errors occur when the DFT is applied. The transformation of Sum(t) → Sum(ω) is, therefore, done by

$$F(\omega) = \frac{1}{i\omega} \frac{(\omega\Delta/2)}{\sin(\omega\Delta/2)} \exp(-i\omega\Delta/2) \times \sum_{n=1}^{N} [[F(n\Delta) \ldots - F(n\Delta - \Delta)] \exp(-i\omega n\Delta)]. \qquad \text{I-84}$$

Truncation errors result when the time domain data end at a finite time instead of continuing infinitely. Truncation errors cause a decrease in the magnitude of the low frequency data and superimpose a sinusoidol oscillation on the high frequency data. An exponential tail may be added to P(t) to decrease these errors and to effectively increase the time window on the oscilloscope to (4 - 7) x τ of the macroscopic dielectric relaxation function.[29,56] The DFT mathematically produces a relaxation at the frequency of (1/time window). It is thus necessary to lengthen the time window on the oscilloscope or add an exponential tail to stop the overlap of the sample and DFT Tau's.

Equation I-84 takes the difference between adjacent data points which amplifies the effect of noise. The initial waveform is signal averaged to increase the Signal/Noise ratio and thereby decrease the effect of random noise. This data is then smoothed by the algorithm

$$SF(n\Delta) = \tfrac{1}{2}\left(\frac{R(n\Delta - \Delta)}{2} + F(n\Delta) + \frac{R(n\Delta + \Delta)}{2}\right).^{29,55} \quad \text{I-85}$$

Since only ratios are used to derive ε^* from the reflections (see equation I-80), the errors introduced by smoothing and by the symmetrical response functions of the sampling circuit are cancelled out. This is because the two sources of error are convoluted with the sample response in the numerator and denominator of the ratio. Limitations of the transforms or any asymmetry in the response of the sampler circuits to forward and returning pulses will cause errors which do not cancel out. An example of asymmetric response is one in which the coaxial cable has both connectors with lower impedance than the cable. As noted above, this yields bouncing reflections. These errors may need to be corrected by use of the bilinear correction factor.

Limitations, Problems, and Corrections

The TDR system has several other limitations besides asymmetrical responses of the equipment. As mentioned earlier, real voltage pulses have risetimes, Tr, which lead to an exponentially decreasing amount of information from the transforms as ω increases, e.g., $L[V_o(t)]$ equals[48,55]

$$V_o = [V_o/(i\omega)^2 Tr][1 - \exp(-i\omega Tr)] . \quad \text{I-86}$$

Drift is the other instrumental problem. It may take three forms: (1) drift in the horizontal position of the displayed

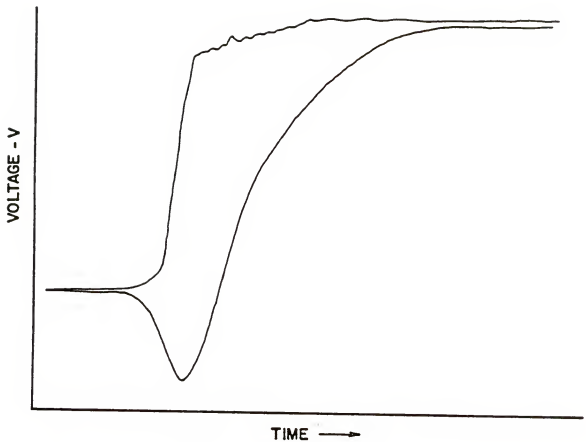
image, (2) drift in the rise time of $V_o(t)$, and (3) drift in the interval between data point acquisitions. The last is equivalent to adding a low-pass filter to the system. The addition of a timing marker to the reference and sample waveforms compensates for the horizontal drift. The zero of $V_o(t)$ and R(t) are then lined up with the timing markers before the transform.[29,54,55] If the horizontal drift is less than an integral number of data points, equation I-82 may be used to compensate for it.

The sample and its packing may cause several problems, including (1) poor electrode contact with a solid sample, (2) conductivity of the sample and polarization of the electrode by the conductive sample, and (3) the sample being non-homogeneous. The first situation leads to a decrease in the detected response from the sample. Conductivity leads to an absorption of energy from the applied electric field and, therefore, affects ε'' (see Figures I-15 - I-17).[29,46,47,48,53] The difference curve, P(t) which equals $V_o(t)$ - R(t), exponentially decays to the base line with a non-conducting sample, but for a conducting sample, P(∞) goes to a non-zero value, i.e.,

$$\frac{P(\infty)}{2V_o} = \frac{\sigma d/ck}{1 + \sigma d/ck} = \frac{G_s}{G_c + G_s}, \qquad \text{I-87}$$

where P(∞) equals P(t) as $t \to \infty$, σ equals the specific conductance of the sample (mho/m), G_s equals the ohmic conductance of sample which equals $(\frac{\sigma}{k})dC_g$, G_c equals the characteristic conductance of the cable, k equals the unit conversion factor e.g., if σ in mho/cm and C in pF then k equals 0.0884 (see Figure I-15 and I-16). The

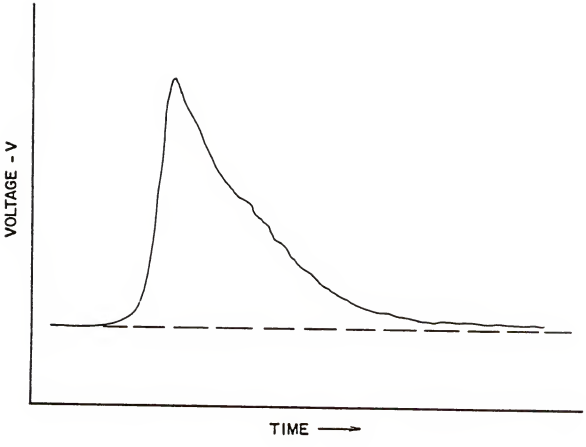
Figure I-15. The oscilloscope trace of $La_{0.8}Sr_{.2}FeO_3$ and air. The long time values of each waveform are not equal to each other since there is conduction through the sample.



$La_{.8}Sr_{.2}FeO_3$

5 NSEC. WINDOW

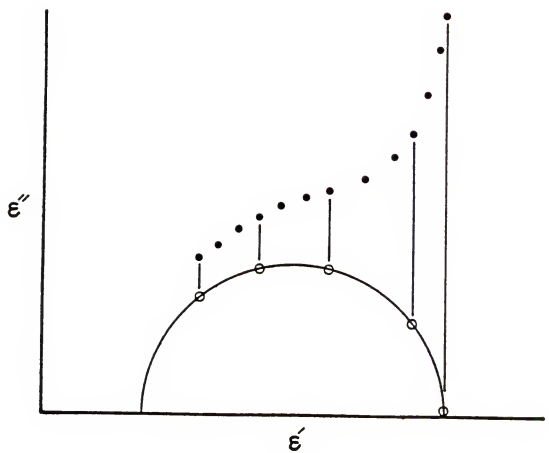
Figure I-16. The difference spectrum, P(t), for $La_{0.8}Sr_{0.2}FeO_3$ versus air. Since the sample has dc conductivity, the value of $P(\infty)$ is not equal to 0, i.e., part of the applied voltage is being "consumed" to drive the electron through to solid. Of special note is the nearly exponential decay of P(t).



$La_{.8}Sr_{.2}FeO_3$

5 NSEC. WINDOW

Figure I-17. Shows the effect of conductivity on the complex permittivity of a Debye dielectric. The filled and open circles represent values before and after correcting for conductivity (using equation I-89). The solid vertical lines connect the points that are at the same frequency.[53] The error becomes worse at the lower frequencies (see equation I-89).


ε″
ε′

former figure is of an oscilloscope trace for air and the 20% by mole fraction doped perovskite, $La_{0.8}Sr_{0.2}FeO_3$, in a 0.5 mm center conductor cell. Figure I-16 is the P(t) curve for this sample. From both figures it can be seen that the voltages of the sample and reference waveforms do not match at long times, e.g., $P(\infty)$ is not equal to 0. Also the nearly exponential decay of the P(t) curve was predicted by theory (see Figure I-12). If one desires to add an exponential tail to the P(t) data, then he would use the last 10 - 20% of this exponential curve to define the parameters for the added exponential tail.

Equation I-87 shows that, as the sample depth is increased, the effect of conductivity also increases. A compromise must therefore be made between increasing the signal strength by increasing the length of the center conductor and the effect of conductivity.

The non-zero value of $P(\infty)$ (see Figure I-16) causes leakage errors with the DFT of P(t). Cole suggests that the Samulon Formula, equation I-84, be applied to the P(t) values derived from a conductive sample or that the maximum frequency be limited by the criteria that f(Z) equal 1 and the use of equation I-88,[29]

$$\varepsilon^* = \frac{c}{d} \frac{[p - (q)\sigma/k]}{i\omega q} , \qquad \text{I-88}$$

where $\sigma = \frac{c}{d} \lim_{t \to \infty} \frac{V_o(t) - R(t)}{V_o(t) + R(t)} = \frac{c}{d} \frac{P(\infty)}{Q(\infty)}$.

This equation is derived from

$$\varepsilon_t^* = \varepsilon^* + \sigma/i\omega k \ , \qquad \text{I-89}$$

where ε_t^* and ε^* equal the total and dipolar dielectric constants, respectively, k equals the conversion factor (σ and ε in esu and ω in sec^{-1}, then k equals 4π or, if σ is in mho/m, $\frac{1}{\omega}$ is psec; then k equals 0.113). In Cole's most recent paper dealing with conductivity, he subtracts the affect of σ.[53] He uses the equations

$$\varepsilon^* = \varepsilon_t^* - \frac{4\pi\sigma}{i\omega} \ , \text{ and} \qquad \text{I-90}$$

$$\sigma = \frac{c}{4\pi d} \frac{P_\infty}{Q_\infty} \ , \qquad \text{I-91}$$

where σ is in esu units and the inner/outer conductor ratios of the sample cell and coaxial cable are the same. The error resulting from having conductivity present is demonstrated in Figure I-17. As this figure shows, the effect worsens at the lower frequencies, and only the ε'' term is affected, i.e., the points with and without correction for conductivity have the same ε' values. The general trend of increasing error in the data at the lower frequencies caused by conductivity is opposite in frequency response from that of propagation error (see Figure I-14).

A sample with large conductivity may also polarize the electrodes, an effect which increases the apparent ε' value at low frequency or causes the R(t) curve to slowly decrease in value with time.[20,48,53]

Having a non-homogeneous sample may also cause distortions.

With solid samples, if there is air between the particles, then ε^* will be decreased by an amount related to how much air is present and the shape of the voids between the particles.

A more serious problem arises from having a conductive impurity in a non-conductive sample. This situation is called the Maxwell-Wagner effect.[20] If the pure sample is a Debye dielectric, then the impure sample will still appear as a Debye dielectric in the experiment, but the observed τ will be less than the actual τ for the pure sample. This situation can be caused by common impurities such as water or metal particles being trapped in the voids between the sample particles.

If an instrumental error, e.g., undesirable impedance mismatches, is consistent, then the error can be corrected by a bilinear calibration of the equipment.[57] The correction factor is based upon network analysis of a two-terminal (one-port) circuit. Cole's[57] analysis is based on the premise that the network is terminated in a known, y_s, and an unknown, y_x, admittance. If the voltage difference between the known and the unknown arms of the circuit is measured by the sampler, then one can solve for the unknown y_x. This value is then used to correct the experimentally measured ε^*.

The bilinear equation used in this work is

$$\varepsilon^* = \frac{A\varepsilon_M^* + C}{1 - B\varepsilon_M^*} , \qquad \text{I-92}$$

where A, B, C, ε_M^* and ε^* are all frequency-dependent complex numbers, ε^* is the corrected or theoretical ε^* of the sample, and

ε_M^* is the measured value of ε^*. Ideally the coefficient B is the short circuit correction factor, i.e., it is the correction factor when y_x equals ∞, while C is an offset term. The inverse of A is ideally the open-circuit voltage transform ratio, e.g., the ratio of voltage at the air-filled cell to that in the coaxial line behind the cell.[45,56,58] The use of this correction factor will be discussed later.

The present TDR equipment gives very good results for the liquid alcohol samples studied in this work. Figures I-18 - I-20 are of n-propanol. These graphs are from the early work of this project and use equation I-73 to analyze the data. They were made before the bilinear correction factor or the base line correction (see the next chapter) was used (see Figures II-3 - II-6) and they are quite similar to the theoretical ones in Figures I-7 - I-8.

Figure I-18 Figure I-18 plots $\varepsilon'(\omega)$ versus ℓn (frequency) for n-propanol. In Figures I-18 - I-20, the sample was acquired before the bilinear correction factor or base line correction was made (see Figures II-3 - II-6).

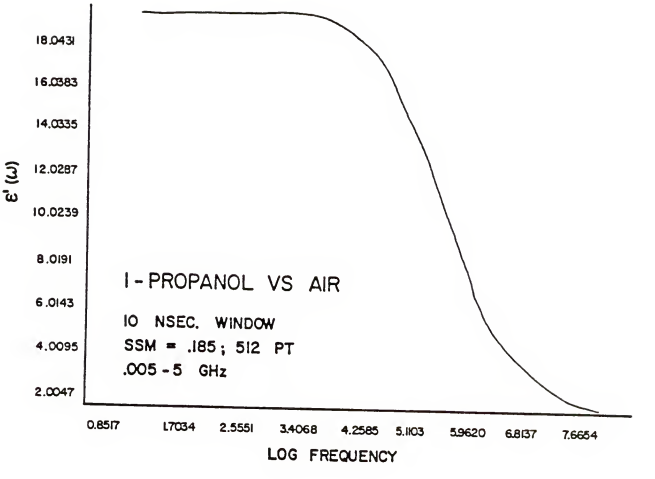

18.0431
16.0383
14.0335
12.0287
10.0239
8.0191
6.0143
4.0095
2.0047
ε' (ω)
1-PROPANOL VS AIR
10 NSEC. WINDOW
SSM = .185; 512 PT
.005-5 GHz
0.8517
1.7034
2.5551
3.4068
4.2585
5.1103
5.9620
6.8137
7.6654
LOG FREQUENCY

Figure I-19. The $\varepsilon''(\omega)$ versus ln (frequency) for n-propanol.

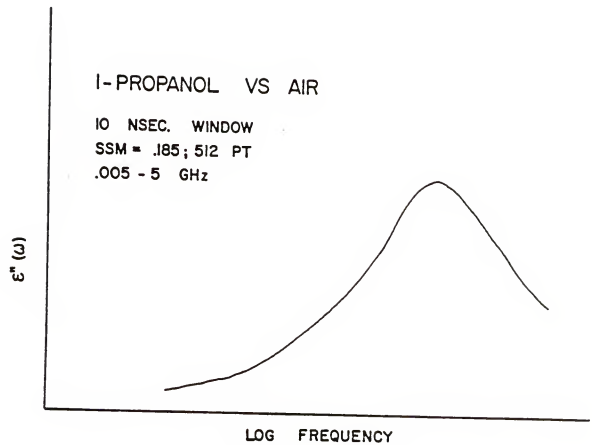
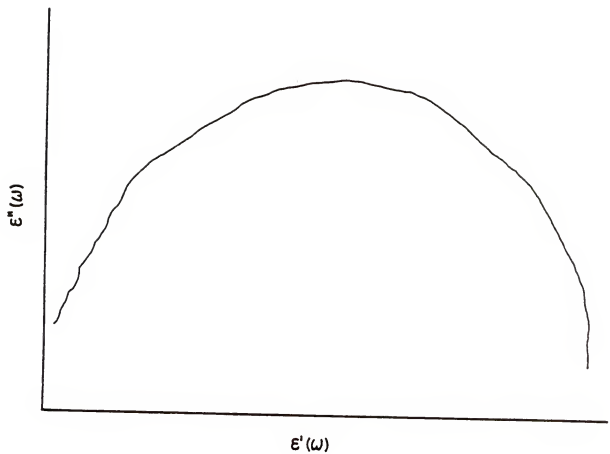

I-PROPANOL VS AIR
10 NSEC. WINDOW
SSM = .185; 512 PT
.005 - 5 GHz
ε" (ω)
LOG FREQUENCY

Figure I-20. The dispersion versus absorption, DISPA, plot for n-propanol.


ε''(ω)
ε'(ω)

CHAPTER II
EXPERIMENTAL SECTION

Introduction

Preparations for the samples used in this experiment were as follows. Reagent grade methanol (Fisher), ammonium hexafluorophosphate (Ozark-Mahoning), calcium acetate • xH_2O (Fisher), sodium acetate (MCB), ruthenium tricloride • xH_2O (Alfa),2,2'-bipyridine, bipy, (Eastman), and Sephadex LH-20, (Sigma) were used without further purification. Potassium hexaflurophosphate (Alfa) was dissolved in a minimal amount of water and filtered before use. Nitrogen saturated solutions were bubbled with N_2 for 20-30 minutes before use. Solvents were degassed by the freeze-pump-thaw method. The tetradentate 2,2'-bibenzimidazole, $BiBzImH_2$, was available in the laboratory and made by the Fieselmann et al. procedure.[59] All other chemicals were reagent grade and used without further purification, unless otherwise specified. All ruthenium complexes were refluxed under N_2 atmospheres.

The ruthenium chloride salts were purified via Sephadex LH-20 size exclusion column chromatography, using an Altex 1 m x 2.5 cm I.D. column. A methanol slurry of 90-100 grams of Sephadex was added to the column. The column had previously been filled by one-third with methanol. After the Sephadex LH-20 had settled

(approximately 4 hrs.), the elusion tube was opened to complete packing. A thin layer of sand was added to the top of the Sephadex to facilitate even distribution of the reaction mixture without disturbing the packing. If the Sephadex LH-20 is new and unexposed to the solvent, it should sit in contact with the methanol for about 1 h before further additions are made to the column; otherwise, it needs only ½ h swelling period before use. Longer swelling periods often lead to poorer packings.

To perform a separation, the compound was dissolved in the minimum amount of methanol; a 1-5 mL aliquot was added to the sand. After all of the sample had entered the sand, the sand and the column above it were washed with a minimal amount of methanol. The reservoir was an approximately 80% filled 500 mL separatory funnel, which was able to maintain the column for 2-4 h. The column was then washed with 4-6 drops of concentrated HCl in 40 mL CH_3OH solution and followed by a 400 ml CH_3OH rinse.

Preparation of Compounds

$FeCl_2 \cdot x$ Hydrate

The compound was made by a modification of preparations found in the current literature.[60,61] Reagent grade $FeCl_2 \cdot xH_2O$ (200 g), electrolytic iron powder (8.5 g, Mallinckrodt, 96%), and 8 - 9 mL of 38% hydrochloric acid were added to 100 mL H_2O. The mixture was stirred under N_2 at room temperature for approximately ½ h, then warmed to 60°C until the solid had dissolved and the solution

had turned bright green. The hot solution was then filtered through a large-diameter, medium-porosity, fritted glass funnel. All filtrations were carried out in a glove bag. The sample was cooled to room temperature and the green crystals, collected by filtration. The solution was capped while in the glove bag and stored at 5°C overnight. This solution was then filtered. The two batches of crystals were combined and vacuumed dry for 6-10 h at 80-85°C to produce the whitish dihydrate or at 160°C for 6-7 h to produce the off-white anhydrous powder.

A slight variation of the above procedure was also used. The green crystals were rinsed with a minimal amount of methanol, followed by diethyl ether. The anhydrous compound was produced by vacuum drying it at 160°C.

It is important to note that 1. technical grade iron powder (Mallinckrodt) produced a very low yield. The main product was a black polymer; 2. if the reagent grade $FeCl_2 \cdot xH_2O$ is sizeably contaminated by ferric compounds, the amount of 38% HCl, iron powder, and heating time will all need to be increased.

$[Fe^{II}Fe^{III}_2(O)(CH_3COO)_6(H_2O)_3] \cdot 1H_2O$

The complex was prepared by methods standardized in the literature.[62] Water (178 mL) and glacial acetic acid (378 ml, 6.3 moles) were mixed. A slurry of $Ca(CH_3COO)_2 \cdot xH_2O$ (111.4 g, 0.03 moles assuming x equals 1) in two thirds of the above acetic acid solution was added to a freshly prepared solution of $FeCl_2 \cdot x\ H_2O$ (0.30 moles), where x equals 0 or 2, in 200 mL water. The slurry

was rinsed into the iron powder mixture with the remaining acetic acid solution. The reaction mixture was aerated and heated at 68 - 71 °C for 6 h. A reflux condenser was attached to minimize evaporation. A N_2 atmosphere was maintained over the solution as it cooled to room temperature. The solution was then stored at 5°C for 2 h. The resulting black solid was collected by filtration in a glove bag and washed with N_2-saturated 0.083M acetic acid. A brown solid was produced from the black solid as it was vacuum dried at room temperature for 2 days. The infrared spectrum in a KBr pellet corresponds to published spectrum.[62,63]

(%Yield = 20-25%, Calculated: C = 23.63, H = 42.9; Found: C = 23.16, H = 4.29)

In this variation, it is important to note (1) that if the final supernatant was stored overnight at 5°C, an amount of black solid will be obtained that is equal to or greater than the amount of solid obtained above. This latter black solid analyzes as the dihydrate after two days of vacuum drying;[63] (2) that the amount of H_2O in the calcium acetate used in this experiment was unknown.

$[Fe^{II}Fe_2{}^{III}(O)(CH_3COO)_6(C_5H_5N)_3](C_5H_5N)_x \cdot yH_2O$

The complex was made by the procedure established by Dzioblowski et al.[62] The preceding complex (1.7 g) was added to 10 mL N_2 saturated pyridine. The resulting solid instantly turned black. After it was stirred for 20-30 minutes, the sample was filtered in a glove bag and then vacuumed dry at room temperature

for 8-12 h. This sample was made from the monohydrate aqua complex instead of the dried complex described in the literature. This change caused water as well as pyridine to be trapped in the lattice.

(% yield = 43-47, Calculated for $[Fe_3(O)(CH_3COO)_6(C_5H_5N)_3](C_5H_5N)_{0.5}$, Calculate:C = 43.49, H = 4.39, N = 6.02; Found:C = 44.42, H = 4.49, N = 6.23)

$[Fe_3(O)(CH_3COO)_3(H_2O)_3]ClO_4 \cdot 2H_2O$

This compound preparation was a modification of a synthesis developed by Dzioblowski et al. [62] Seventy percent $HClO_4$ (53 mL, 0.6 moles) was added at a rate of 1 drop/3-4 seconds from an addition funnel into a stirring solution of electrolytic iron metal powder (11.2 g, 0.2 moles) in 90 ml H_2O. The mixture was warmed to 40-45°C for 1 h. The solution was cooled to room temperature, then filtered to remove any unreacted material. The resulting green solution was cooled and maintained at 5-10°C. Thirty milliliters of 15% H_2O_2 were added to the stirring solution via the addition funnel. The solution was then cooled to and maintained at 5°C. Anhydrous sodium acetate was slowly added (32.8 g, 0.4 mole) to the stirring solution, all of which was then placed under a gentle flow of N_2 for 3 days. Two thirds of the liquid evaporated during this period. The red-brown sample was filtered, washed with two 25 mL portions of approximately 5 °C water, and then blotted with filter paper. Portions to be used were vacuum dried at room temperature for 20 h.

4,4'-Dimethoxy-2,2'-bipyridine

This item needs to be prepared in a good hood while the researcher wears a particle filter mask and gloves. The complex was prepared by literature preparations.[8,64,65] Glacial acetic acid (125 mL), 30% hydrogen peroxide (25 mL), and 2-2'-bipyridine (25.0 g) were heated in a water bath at 100 °C for 4 h. The sample was cooled to room temperature and another 25 ml portion of H_2O_2 was added. The solution was heated for 4 more h at 100 °C. The solution was cooled to 0 °C, after which it was neutralized with a minimal amount of cold 25% sodium hydroxide. The impure white precipitate of 1,1'-di-N-oxide-2,2'-bipyridine was collected by filtration, washed with small portions of water, and recrystallized from water. The sample was vacuum-dried.

Concentrated sulfuric acid (100 mL), fuming nitric acid (100 ml), and the above compound were heated in a water bath at 100 °C for 8 h. The yellow solution was cooled and poured over crushed ice (400 g) and then neutralized with a minimum amount of cold 25% aqueous sodium hydroxide. Upon neutralization, the solution turned orange. The impure yellow 4,4'-dinitro-1,1'-di-N-oxide-2,2'-bipyridine formed was collected by filtration, washed first with water, and then with two 50 mL washes of hot absolute ethanol. The sample was dried under vacuum.

Metallic sodium (2.85 g, cleaned in methanol) in 380 mL methanol was added to the preceding crude compound. The suspension was stirred for 3.25 h while the temperature was maintained at 33 ±

2 °C in a water bath. The solution was cooled to 0 °C, neutralized with a minimal amount of concentrated sulfuric acid, and filtered; the white precipate was discarded. The solvent was removed via a rotary evaporator. The solid was extracted by stirring the sample with three separate 300 mL portions of hot chloroform. The chloroform extracts were combined, refluxed for ten minutes with activated carbon (5 g), and filtered. The volume was reduced to 500 mL by distillation. Impure 4,4'-dimethyl-1,1'- di-N-oxide-2,2'-bipyridine was produced by adding hot petroleum ether (300 mL, 70 - 110 °C) to the solution.

This compound was mixed with 68 mL of dry chloroform and cooled to -3 °C. Phosphorus trichloride (10.8 mL) was added, and the suspension was refluxed for 3/4 h, cooled, and poured onto crushed ice (100 g). The chloroform phase was extracted with four 50-mL portions of water. All 5 aqueous extracts were combined. Neutralization with 25% sodium hydroxide caused a bulky white precipitate to form. The solution was cooled, and the white solid was collected by filtration and washed with water. The sample was then recrystallized from absolute ethanol. The total percent yield for the complete synthesis was 5-7 percent (mp = 170-172°C, Lit = 170-172°C [66]).

$[Ru(II)(R_2 - bipy)_2Cl_2]$

This is a general preparation for the bis complex when the R substituent is not affected by refluxing the sample in alcohols.

A ratio of 1.8:1 to 2.0:1 by mole of $RuCl_3 \cdot xH_2O$ was refluxed

in (25 mL) 4:1 (v/v) ethylene glycol/absolute ethanol for 3 h. The volume was decreased to near dryness under vacuum at 80 - 100 C.* The sample was then refluxed for 1 h in (25 mL) of 50/50 (v/v) ethanol/water. It should be filtered while hot and then allowed to cool. Next (8 - 10 g) of LiCl was added to the room temperature solution and distilled off the ethanol until it reached 90 °C. The round bottom was capped while hot and stored at -5 °C for 3 h. It was next filtered and then washed with small aliquots of 0 - 5 °C water until the color of the tris R_2 - bipy ruthenium (II) chloride salt stops filtering through. If the tris complex is luminescent, a black light may be helpful in determining when the tris complex is removed. The sample was dried for 8 - 12 h under vacuum at 44 - 50 °C. Percent yields ranged from 60 - 85%.

The amounts given in ( ) are the amounts which yield the best results for typical $RuCl_3 \cdot x\ H_2O$ sample sizes of 0.1 - 0.2 grams.

*The yields in some cases may be increased by extracting the excess ligand out of the crude sample with toluene at this point.

$[Ru(II)(4,4' - CH_3O)_2 - bipy)_2Cl_2]$

To 25 mL of the mixed alcohol solvent, $(4,4' - CH_3O)_2$ - bipy (0.225 g, 1.04 mmoles) and $RuCl_3 \cdot 3H_2O$ (0.150 g, .573 mmoles) were added. (% yield = 60%)

$[Ru(II)(bipy)_2Cl_2]$

The ligand (0.310 g, 1.99 mmoles) and $RuCl_3 \cdot 3H_2O$ (0.260 g, 0.99 mmoles) were used. (% yield = 85%)

$[Ru(II)(bipy)_2(BiBzImH_2)]Cl_2$

The complex was made by a modification of a preparation found in the literature.[67] A 1.5:1 mole ratio of $[Ru(II)(bipy)_2Cl_2]$ (0.483 g, 0.99 mmoles) to the crude $BiBzImH_2$ (0.354 g, 1.52 mmoles) was refluxed in 20 ml absolute ethanol for 18 h.‡ The solvent was removed under vacuum. The compound was then purified on the Sephadex LH-20 column by collecting the leading fluorescent red-orange band. The last step was repeated until the desired band was isolated. The sample was vacuum dried at 44 °C for 8 - 12 h.

‡The reaction rate can be considerably increased by adding 0.5 to 1 mL H_2O to the absolute ethanol while the sample is refluxing (% yield = 69%).

$[((4,4' - CH_3O)_2 - bipy)_2Ru(II)(BiBzIm)Ru(II)(bipy)_2]Cl_2$

The complex was made by a modification of a preparation described by Haga.[67] $[Ru(II)(bipy)_2(BiBzImH_2)]Cl_2$ (0.101 g, 0.168 mmoles) was added to 20 mL absolute ethanol. An 8:1 mole ratio of triethyl amine, Et_3N (density equals 0.7275 g/ml) was added to the $BiBzImH_2$ complex in solution. The solution changed to a violet color upon the addition of the base. It was then stirred for ten minutes before $[Ru(II)((4,4' - CH_3O)_2 - bipy)_2Cl_2]$ (0.118 g, 0.165 mmoles) was

mmoles) was added. The solution was refluxed for 2 h and another aliquot of the base (12:1 mole ratio) was added. The solution was refluxed for an additional 22 h. The sample was purified by several passes through the Sephadex LH-20 column. The leading red-purple band was collected.

It should be noted that 1. an attempt was made to separate the partially deprotonated starting material (the second band on the Sephadex LH-20 column) from the dimer by Silica gel-TLC plates. Different ratios of the following eight solvents were tried: a. ethyl acetate/low boiling petroleum ether, b. ethyl acetate/methanol, c. methanol/DMF, d. methanol/DMSO, e. methanol/water, f. methanol/DMF/DMSO, g. water, and h. methanol. All of these solvent mixtures were tried, with and without the addition of various amounts of triethyl amine. In all cases the separation was poor.

2. A better separation of the products is likely if ion exchange column chromatography with a basic solvent (e.g., CH_3OH/Et_3N) is used. Also, the separation will be improved if a 2 m Sephadex LH-20 column is used instead of the 1 m column presently used.

3. Better separation on the Sephadex LH-20 column is possible if part of the excess ligand is extracted from the impure sample with warm toluene before the first application of the impure sample to the Sephadex LH-20 column.

(CHN analysis gave irreproducible results for this sample.)

$[(bipy)_2Ru(II)(BiBzIm)Ru(II)(bipy)_2]Cl_2$

This was made by modification of the Haga preparation.[67] $[Ru(II)(bipy)_2Cl_2]$ (0.463 g, 0.956 mmoles) and $BiBzImH_2$ (0.359 g, 1.55 mmoles) were added to 20 mL absolute ethanol and 2 mL H_2O. The solution was refluxed until it maintained a constant red color; this normally required from 4 - 8 h. The solution was vacuum-dried.‡ The resulting solid was added to 20 mL absolute ethanol. After 5 to 10 minutes of stirring, an 8:1 mole ratio of Et_3N: crude $BiBzImH_2$ complex was added. The sample was stirred for another 10 minutes, and then a slight excess of $[Ru(II)(bipy)_2Cl_2]$ (0.465 g, 0.961 mmoles) was added. The solution was refluxed for an additional 2 h. Another portion of Et_3N (12:1 mole ratio) was added and then refluxed for 3 h. The sample was vacuum-dried and purified as with the above dimer. There were three overlapping bands on the Sephadex LH-20 column: red-purple, brown, and red-purple; the leading band was collected. The amount of the brown band varied from preparation to preparation.

‡The final purification can be made considerably more simple if the crude vacuum-dried monomer is purified by at least one pass through the Sephadex LH-20 column before the addition of $[Ru(II)(bipy)_2Cl_2]$ (see note 3 in the above preparation).

One should note that the sample is very likely air oxidizable since an overlapping brown band (similar to one mentioned above) on the Sephadex LH-20 column was produced when the previously purified sample had been exposed to air for a few days.

(CHN analysis gave irreproducible results for this sample.)

$[(bipy)_2Ru(II)(BiBzIm)Ru(III)(bipy)_2](PF_6)_5$

The mixed-valence ruthenium dimer was made by adding a stoichiometric amount of $(NH_4)_2(Ce(NO_3)_6)$ in 1M HCl to the dimer dissolved in a minimal volume of deoxygenated water in a glove bag. Saturated NH_4PF_6 in deoxygenated water was then added to precipitate the compound. The comproportionation constant for the dimer is greater than $10^{4.8}$

(CHN analysis gave irreproducible results for this sample.)

TDR Instrumentation and Techniques

Introduction

The following TDR equipment was obtained from Tektronix Inc.: a 7854 digitizing oscilloscope with extra memory; a 1-nsec rigid coaxial cable; a 7S12 TDR/Sampler plug in module which contains an S-52 pulse generating head (T_r < 25 psec, 200 mV into a 50. Ω load) and an S-6 sampling head (T_r < 30 psec, ± 1V); and a 7S11 sampling unit module with an S-6 sampling head. Three Gore, Inc., type 3 flexible coaxial cable (0.290 inch diameter, SMA connectors; two 72.0 inch and one 78.0 inch in length) were used. Equipment purchased from Midwest Microwave Inc. included a directional coupler (7-18 GHz, 10 dB, Model 5015), an SMA Female/SMA Female connector (DC-18.0 GHz, Model 2595), and a 7 mm SMA Male Rebuilt Kit (DC-18.0 GHz, Model 2542). (See Figure I-9 and II-1, II-2 for diagrams of the equipment design.) An IBM CS-9000 computer with dual 8-inch floppy disks and a 10-megabite hard disk was interfaced with the digitizing oscilloscope. The IBM CS-

Figure II-1. Diagram of the temperature control equipment. Dinitrogen gas is passed through two copper coils submerged in liquid N_2 or dry ice/acetone for cooling. The cooled N_2 gas is then circulated through a copper coil surrounding the sample (see blow-up of sample dewar - Figure II-2). The temperature is maintained by a feedback system which controls the heating of the heat tape in the sample dewar (Figure II-2). The sample and all cooled cables are in a glovebag which minimizes ice formation on the sample and the cables.

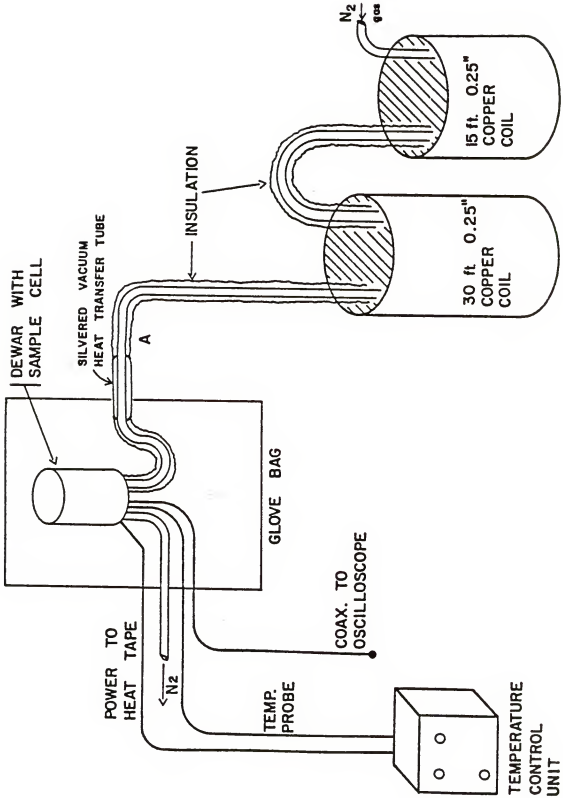
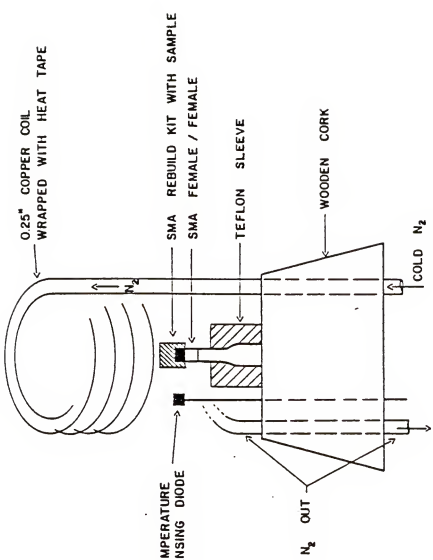

DEWAR WITH SAMPLE CELL
SILVERED VACUUM HEAT TRANSFER TUBE
A
INSULATION
GLOVE BAG
POWER TO HEAT TAPE
N2
TEMP. PROBE
COAX. TO OSCILLOSCOPE
TEMPERATURE CONTROL UNIT
30 ft. 0.25" COPPER COIL
15 ft. 0.25" COPPER COIL
N2 gas

Figure II-2. Blow up of sample dewar in Figure II-1. The temperature-sensing diode is placed between the copper coils and the sample. A teflon sleeve is used to hold the sample and cable in a vertical position.


0.25" COPPER COIL
WRAPPED WITH HEAT TAPE
N_2
SMA REBUILD KIT WITH SAMPLE
SMA FEMALE / FEMALE
TEFLON SLEEVE
WOODEN CORK
COLD N_2
TEMPERATURE
SENSING DIODE
N_2 OUT

9000 computer was interfaced into the Quantum Theory Project's 11/780 VAX computer, VAX. The temperature control unit was designed and built by Steve Miles of the University of Florida Chemistry Department Electronic Shop (see Figure II-1). It includes a temperature probe with a type 1N914 silicon diode and a 40 V variac. It controls the heating of the sample. The sample is held vertically in an inverted dewar (see Figure II-2). The sample cell and the temperature probe are surrounded by a copper coil wrapped with heat tape. The heat transfer tube (see point A in Figure II-1), has an inner diameter which equals $\frac{1}{4}$ inch and is under a reduced pressure of 10^{-5}-10^{-6} Torr. The tube was silvered by a modified Tolen's test[68] and evacuated for four days on the vacuum line.

For studies taken below room temperature, both dewars at the right side of Figure II-1 were filled with liquid N_2 to obtain the lowest temperatures; for other results, the first dewar with the 15 ft. coil was filled with dry ice - acetone, slowing the boiling off of the liquid N_2 in the second dewar. To maintain the desired temperature, heat was applied via the heat tape in the sample dewar. The variac in the temperature contol unit was calibrated to minimize overshoot for the desired temperature. To obtain the lowest temperatures, the insulated copper coil was disconnected from the silvered glass vacuum heat transfer-tube, and the coil from the second dewar (at Point A in Figure II-1) was inserted directly into the sample dewar, i.e., the copper coil and heat tape surrounding the sample were removed, allowing the cold N_2 to fill

the sample dewar directly. A sample dewar that should give a larger range of temperatures will be described later.

There were 3 sample cells. Their dimensions were: inner diameter equaling 6.9 mm; total depth 6.7 mm; inner conductor diameter, 3.0 mm. The outer conducter was stainless steel. The three cells had different inner brass conductor heights: 0.5 mm, 1.5 mm, and 4.3 mm. The longer center conductors were used with samples having smaller ε'. Two Teflon plungers (outer diameters equaling 0.7 mm) were made by the machine shop. One had a center hole to fit around the center conductor of the sample cell. Threaded brass caps that fit the threading on the sample cells were also made. The caps had various brass inserts of 1.9, 2.8, 3.0, 3.7, 4.4, 4.9, and 5.4 mm. These were used to pack the solid samples to various depths.

Basic Operation

The equipment was connected as shown in Figures I-9, II-1, and II-2 with the following modifications: When a timing marker was used, the 78 inch coaxial cable connected the S-52 pulse generating head and the S-6 sampling head, while the 1 nsec cable connected the S-6 sampling head to the direction coupler. The main lead of the directional coupler connected to the 72-inch cable going to the sample cell. The other lead of the directional coupler was connected to an open-ended coaxial line cut so that the reflections from its open end would appear about one division before the rapid rise resulting from the sample-cell signal on the digitizing

oscilloscope. The 1 nsec line and the directional coupler were removed from the above set-up if no timing marker was used.

After the connections were made, the digitizing oscilloscope (called simply an "oscilloscope" from here on) warmed up for at least 12 hours, and all connections doubled checked, then the procedure below was used to perform TDR. It can be followed to repeat the results.

1. The first step involved packing the sample cell.

a. If a liquid is being studied, it should be added with a disposable pipette to a depth of at least 2 mm above the top of the center pin.

b. Solid samples need to be fine powders to pack well; the same depth criterion for liquid samples applies to them. If the sample is air sensitive, the packing should be carried out in a glove bag or a glove box. The SMA Male Rebuild Kit, which is the sample cell, was removed from the coaxial cable to aid in packing the sample. A small amount of the sample was added to the sample cell and then packed down with the one-hole Teflon plunger. This process was repeated until the sample covered the center conductor. From this point on, the sample was packed using either the solid Teflon plunger or the screw-on brass cap. The cap was fitted with the desired insert before packing began. (To obtain the tightest packings, the brass cap should be used to pack down at least the last few additions of the sample to the cell.) Tight packing is essential to minimize the effects of voids between the sample particles and to ensure that the center brass pin and its

Teflon holder are completely seated within the SMA Male Rebuild Kit when the sample cell is attached to the coaxial cable. If they are not seated properly, non-reproducible joint reflections will be produced. After the sample cell is secured on the coaxial cable, the brass cap should be carefully removed so as not to disturb the sample cell. It is essential that the cell not be loosened from the coaxial line when the cap is removed.

2. After the cell was packed the TEKEX13.BAS program was loaded.

a. The number of points per time window, P/W, on the oscilloscope was set to 1024 or 512.

b. The Service Request operation on the oscilloscope was disabled by sending the message "RQSOFF" over the IEEE parallel port. (See item 8, Note 1 below).

c. One hundred fifty, 150, averages of reference and sample were acquired on the oscilloscope and stored in the second and third waveform memory locations, 2 WFM and 3 WFM, respectively.

3. Either TEKEX13.BAS or TEKSEND2.BAS were used to transfer the reference and sample waveforms to the IBM CS-9000 computer.

4. The waveform data or any text file was sent to or from the VAX computer via the programs TALK9.BAS. (See item 8, Note 2 below).

5. While using the VAX computer, the time domain data was transformed into the frequency domain data via the program KDSAM9E.FOR. (If needed, the bilinear correction maybe carried out on the VAX computer by using the combination of COLE26.FOR [producing the coefficient A, B, and C - see equation I-92 and the next section] and ICOLE26.FOR).

6. The frequency domain data was graphed and analyzed for f_c, ε_∞, and ε_s, on the IBM CS-9000 computer by the program GRAPH7D.BAS. The original time domain data, or the difference curve, P(t), which is produced by the DIFFER2.FOR program, was graphed by using GRSCOPE2.BAS program.

7. Using TEKEX13.BAS, the Service Request option on the oscilloscope was re-enabled by sending the message "RQSON" to the oscilloscope.

8. Note 1. If the parallel port connecting the oscilloscope to the IBM CS-9000 computer is activated from BASIC, and the IBM CS-9000 computer is returned to the operating system, and the port is later reactivated by the BASIC programs TEKEX13.BAS or TEKSEND3.BAS, then a "Service Request" may be sent to the oscilloscope. This unrequested message locks up both the IBM CS-9000 computer and the oscilloscope. If the Service Request option is disabled on the oscilloscope, this problem is eliminated.

Note 2. Users of TALK9.BAS should always set the default disk drive to a floppy disk instead of a hard disk. This will ensure that any file sent from the VAX computer to the IBM CS-9000 computer will be initially stored on a floppy disk instead of a hard disk. If transmission is broken by the command "Control Alternate Delete" while a file is being sent from the Vax computer to the IBM CS-9000 computer for storage, the disk receiving the file may become corrupted if the IBM CS-9000 computer is a version preceding 1.3. In fact, the complete contents of the disk may become inaccessible if the "corruption" happens near the beginning

of the disk. Thus, to minimize the possible losses, users should always receive the data from the VAX computer on a floppy disk instead of the hard disk.

Efficiency Optimization

This section is composed of two parts. The first involves instrumental optimization while the second presents program/instrumentation optimizations.

Instrumental Optimization

a. To give consistently reproducible results, the oscilloscope needs to be warmed up for at least 12 hours before use.

b. If any settings on the 7S12 TDR/Sampler (a plug-in module in the 7854 digitizing oscilloscope) are adjusted, then the oscilloscope should be allowed 20 minutes to re-equilibrate before use.

c. A compromise between Signal/Noise improvement by signal averaging and drift must be made. Several combinations of the number of points per time window, P/W, and the number of waveforms averaged within the oscilloscope were tested by using air as the reference and sample to find the optimum compromise. The combinations tried were: 1. P/W = 512, with the number of averages equal to 50, 75, 50, 150, 200, 300; 2. P/W = 1024, the number of averages = 75, 150, 200, 300. When P/W = 512, 300 averages (24 seconds acquisition and signal averaging time) gave the best

results; when P/W = 1024, 150 averages (22 seconds acquisition and signal averaging time) did so. When high time domain resolution is desired, e.g., when the reflections from the sample cause only a small initial dip (i.e., R1 of Figure I-9) on the oscilloscope and there is rapid rise to the maximum voltage [e.g., ε_∞ and $(\varepsilon_o - \varepsilon_\infty)$ are small], then one should set the P/W to 1024 or go to a shorter time window. If the sample has dc conductance, then the time window must be long enough to allow P(t), at t equal to the time of the time window, to obtain a constant value. An advantage of using the DFT, the Discrete Fourier Transform, instead of the FFT, the Fast Fourier Transform, to transform the time domain data is that increasing the time domain resolution does not decrease the frequency domain resolution.[69] The time domain resolution is increased by increasing P/W for a given time window.

For the mixed-valence samples used in this work, and at time windows of 2, 5, and 10 nsec, the P/W setting of 1024 gave better results than when P/W equaled 512.

d. The rate of scanning of the waveforms also affects the quality of the results. The best results were obtained with the rate set near the middle of its range.

e. If a timing marker is not used, the reference and sample should be taken as close in time as possible to minimize errors resulting from drift.

f. The openings for the plug-in modules in the 7854 digitizing oscilloscope need to be covered e.g., with cardboard, to minimize air currents passing through the 7S12 TDR/Sampler plug-in

module. This precaution will minimize one source of drift resulting from temperature changes.

Program/Instrumentation Optimization

a. The first third of the points in the first division of the oscilloscope trace were incorrectly assigned. In the P(t) curve, this misassignment of values by the oscilloscope caused a rapid rise or fall resembling a $\delta(t)$ function of magnitude between 0 mV to about 5 mV. In the latter case, the high frequency data were at least damaged, if not destroyed, by the error in the time domain since frequency components were added by the Fourier transforming of the $\delta(t)$ function. (The Fourier transform of a $\delta(t)$ function contains all frequencies.)

The programs KDSAM9E.FOR and DIFFER2.FOR assigned these first points the average base line value, which did not include in its average the first third of the first division points. (See Figure II-3 and Figure II-4 for examples of ε' versus the natural logarithm of frequency, ln (frequency), for air as the sample versus air as the reference before and after this time domain correction was made.) The graph of ε' versus ln (frequency) should have been a straight line since ε' is approximately equal to 1 for air. In the uncorrected version, the graph was obviously far from linear.

The measured value of ε_s for air was increased from 0.87 - 0.9, as in Figures II-3 and II-4, to 1.00 ± 0.01. The latter value was much closer to the correct value. An increase in the length of

Figure II-3. Demonstrates the sizable distortion of the ε' versus ln (frequency) curve for air versus air when the initial part of the base line is misassigned by the oscilloscope (see Figure II-4 for the corrected spectrum). This example demonstrates that seemingly small errors or distortions in the time domain can produce large errors in the frequency domain.

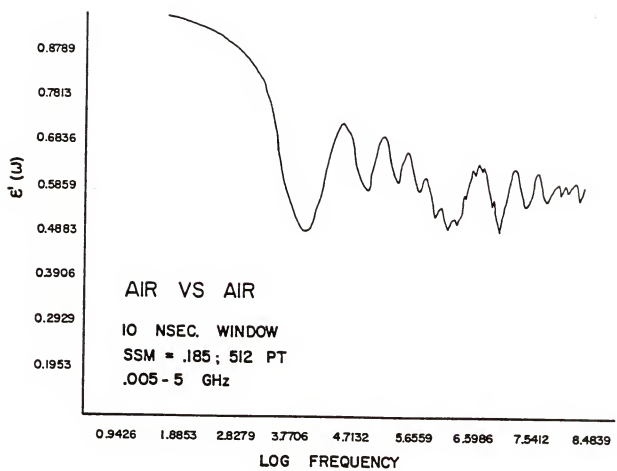
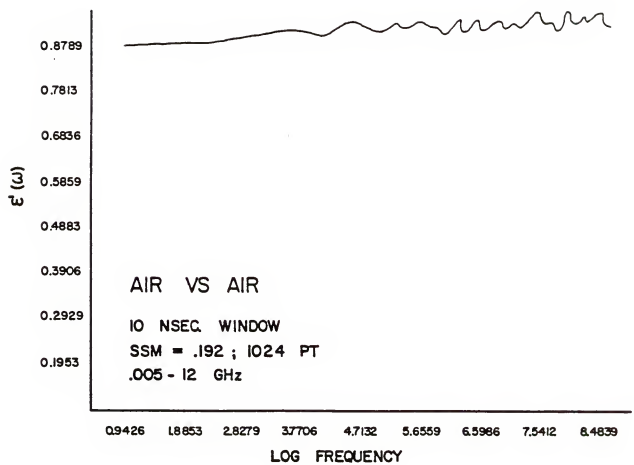

0.8789
0.7813
0.6836
0.5859
0.4883
0.3906
0.2929
0.1953
ε' (ω)
AIR VS AIR
10 NSEC. WINDOW
SSM = .185; 512 PT
.005 - 5 GHz
0.9426
1.8853
2.8279
3.7706
4.7132
5.6559
6.5986
7.5412
8.4839
LOG FREQUENCY

Figure II-4. The same sample as in Figure II-3 except that the base line has been corrected.


0.8789
0.7813
0.6836
0.5859
0.4883
0.3906
0.2929
0.1953
ε' (ω)
AIR VS AIR
10 NSEC. WINDOW
SSM = .192 ; 1024 PT
.005 - 12 GHz
0.9426
1.8853
2.8279
3.7706
4.7132
5.6559
6.5986
7.5412
8.4839
LOG FREQUENCY

the inner conductor of the sample cell from 1.5 to 5.2 mm caused the difference in the two sets of values. This increase is a way of improving the accuracy of the measured value of ε_s for a sample with a small value of ε_s by changing the sample cell dimensions.

b. The timing marker should be aligned within the last third of the first division on the oscilloscope. Also, the timing marker should be set approximately one division before the rapid rise of the reference waveform. The first criterion is set to eliminate the possibility that the timing marker will drift into the region on screen where the oscilloscope misassigns the values of the points. The second criterion is given to ensure that there are enough points between the timing marker and the sample waveform to obtain an accurate base line value. The timing marker also distorts the base line, but this distortion is smoothed before P(t) or Q(t) waveforms are calculated in the programs KDSAM9E.FOR and DIFFER2.FOR.

c. The bilinear correction equation for impedance mismatches may be used. The equation used in this work is rewritten below

$$\varepsilon_T^* = \frac{A\varepsilon_M^* + C}{1 - B\varepsilon_M^*}, \qquad \text{I-92}$$

where ε_T^* equals the theoretical value or the corrected value of ε^* and ε_M^* equals the measured value. Two other forms were also tried.

$$(\varepsilon_T^* - 1) = \frac{A(\varepsilon_M^* - 1)}{1 - B(\varepsilon_M^* - 1)} \qquad \text{II-1}$$

$$(\varepsilon_T^* - 1) = \frac{A(\varepsilon_M^* - 1) + C}{1 - B(\varepsilon_M^* - 1)} \qquad \text{II-2}$$

The equation II-1 failed to give reasonable values of ε_T^* above 1 GHz for the solvents tried. (See Table I for a list of the these solvents.) The equations I-92 and II-2 gave similar results.

To solve for the complex coefficients A, B, and C, one acquires ε^* data (program KDSAM9E.FOR) for three standards of known ε^* values which have only one Debye relaxation in the frequency region that is being studied. [56] The three unknowns, A, B, and C, at each frequency, are then solved by 3 simultaneous equations (see below). The standards chosen should be such that the change in ε' is small over the frequency range of interest, thus minimizing errors resulting from the inaccuracies in the temperature measurements of the standards. Also, if one of the standards is air (ε' approximately equal to 1), then a more accurate determination of the coefficient C can be made (see equations II-2 and I-92 above). In fact, the results in this study were dramatically improved when the third standard chosen was air instead of another material.

Equation I-92 can be rearranged to give

$$\varepsilon_T^* = A\varepsilon_M^* + \varepsilon_T^* B\varepsilon_M^* + C \; . \qquad \text{II-3}$$

This form of the equation was used here to solve for the three complex coefficients. The theoretical values of ε_T^* for each standard are calculated by using equations I-47b and I-47c. An

Table 1

Dielectric Constants for Selected Solvents

Standard	ε_s	ε_∞	α[a]	τ(nsec)[b]	
DMA[25,c,d,e]	38.6		5.0	--	0.015_{000}
Water[f,g]	78.5[25,g,k]		5.2	--	0.0094_{432}[h]
Acetone[20,f]	21.2		1.9	--	0.0033_{423}[h]
Propanol[25,f]	20.1		3.23	0.03	0.37_{136}[h]
Ethyl Acetate[20,f]	6.04		2.48	0.06	0.0043_{502}[h]
Diethyl Ether[25,f]	4.24		1.82	--	0.0021_{751}[h]
Benzene[20,j,i,f]	2.284		1.5[k]	--	0.0063_{662}[h]

a.[f] $$\varepsilon^* = \frac{\varepsilon_o - \varepsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}}$$

b. The accuracy does not warrant five significant figures, but to minimize rounding errors in the computer computations the τ's are entered in the form given here.

c. N,N-Dimethyl Acetamide (Sigma, dried over 4Å sieves).

d. Reference 53.

e. Superscript numbers are the temperature of the data.

f. Reference 70.

g. Values derived from average of 20° and 30°C data.

h. τ is derived from λ_c data by $\tau(\text{nsec}) = \frac{\lambda_c(\text{cm})}{188.49556}$.

i. Additional data in Reference 71.

j. Dried over sodium by W. K. Holley

k. Reference 72.

attempt was then made to solve for A, B, and C by using the matrix

$$\begin{vmatrix} E1 & T1E1 & 1 \\ E2 & T2E2 & 1 \\ E3 & T3E3 & 1 \end{vmatrix} = \begin{vmatrix} T1 \\ T2 \\ T3 \end{vmatrix}, \qquad \text{II-4}$$

where E1 and T1 are the ε_M^* and ε_T^* of standard 1, respectively. There are analogous symbols for standards 2 and 3. The matrix was calculated in FORTRAN by single-precision complex numbers and double-precision arithmetic. In both situations, the error in the frequencies above 1 GHz was too large to suit the purposes of the experiment.

The same set of equations that lead to equations II-4 can be solved algebraically for A,B,and C. The equations used by Kroeger are[56]

$$B = \frac{[E1 - E3][T1 - T2] - [E1 - E2][T1 - T3]}{[E1 - E3][T1E2 - T2E2] - [E1 - E2][T1E1 - T3E3]}, \qquad \text{II-5}$$

$$A = \frac{B \times [T3E3 - T2E2] + [T2 - T3]}{[E2 - E3]}, \qquad \text{II-6}$$

$$C = T1 - [B \times T1E1] - [A \times E1]. \qquad \text{II-7}$$

These were again solved by using single-precision complex numbers

and double precision arithmetic. When the calculations are done on the VAX computer, the single precision complex program usually gives satifactory results. If one needs more accuracy in the higher frequencies, then the double precision version should be used with the following modifications

$$B = \frac{(\delta E1 - \delta E3) \times (\delta T1 - \delta T2) \quad -}{(\delta E1 - \delta E3) \times (\delta T1E1 - \delta T2E2) \; -} \cdots \qquad \text{II-8}$$

$$A = \frac{\dfrac{(\delta E1 - \delta E2) \times (\delta T1 - \delta T3)}{(\delta E1 - \delta E2) \times (\delta T1E1 - \delta T3E3)} \,, \quad B \times (\delta T3E3 - \delta T2E2) + (\delta T2 - \delta T3)}{(\delta E2 - \delta E3)} \,, \qquad \text{II-9}$$

$$C = \frac{\delta T1 - (B \times \delta T1E1) - (\delta A \times E1)}{\delta} \,, \qquad \text{II-10}$$

where δ equals 1×10^6 and a δ preceding a variable implies that δ is multiplied times the variable, e.g., $\delta E1$ equals $(1 \times 10^6) \times E1$.

The best results from the bilinear equation are obtained if the sample with the largest ε' value is used as the first standard and air is used as the third. (See Table 1 for a list of solvents and pertinent data used to obtain A,B,and C.) In the course of this experiment, numerous combinations of the seven standards were tried, all in groups of three. The combination that gave the best results in the frequency range of 5 MHz to 5 GHz was one in which standard 1 was acetone, standard 2 was ethyl acetate, and standard 3 was air.

Figures II-5 and II-6 are of ε' versus ln (frequency) for acetone. The two graphs show the acetone before and after the bilinear correction was applied, respectively. The improvement in

Figure II-5. The ε' versus ln (frequency) for acetone as it appears uncorrected. Notice the rapid and jagged drop in the magnitude of ε' as the higher frequencies are approached.

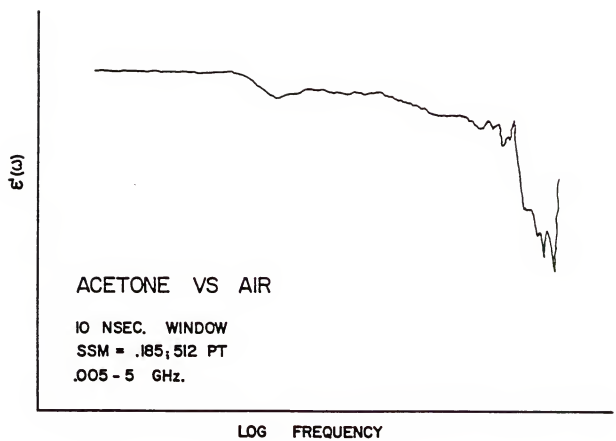
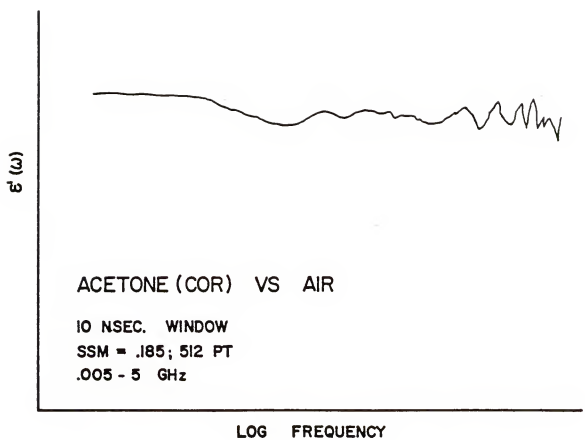

ε'(ω)
ACETONE VS AIR
10 NSEC. WINDOW
SSM = .185; 512 PT
.005 - 5 GHz.
LOG FREQUENCY

Figure II-6. The same sample as in Figure II-5 except that the bilinear correction factor has been applied. The three standards used were DMA, n-propanol, and air.


ε' (ω)
ACETONE (COR) VS AIR
10 NSEC. WINDOW
SSM = .185; 512 PT
.005 - 5 GHz
LOG FREQUENCY

the higher frequency region in Figure II-6 is significant. This is an early trial of the bilinear correction factor, using DMA, propanol, and air as standards. Using the three suggested standards, the experiments achieved much better results from the bilinear correction equations.

d. A program was written that instructed the oscilloscope to acquire the unaveraged waveform, transfer the waveform to the IBM CS-9000 computer, then acquire another waveform. This process was repeated until the specified number of waveforms to be averaged in the IBM CS-9000 computer were collected. The program would then locate the timing markers of the individual waveforms, line up the waveforms correctly, and average them. Unfortunately, this transfer process takes approximately four seconds. The time delay allowed error resulting from drift, e.g., in the risetime, to become sizable. Thus the total error resulting from drift while signal-averaging was less when the waveforms were averaged within the oscilloscope than when they were sent to the IBM CS-9000 computer and individually averaged there. The time for signal averaging on the oscilloscope should be less than 30 seconds to give best results.

e. A simulation program, INVERSE.FOR, written by Doan[30] was modified to yield INVD3.FOR in this work. In an attempt to correct for leakage errors,[29,69,73] several schemes were tried, including (1) the Samuelon equation[29] (see equation I-84); (2) the Nicolson Ramp function,[29,74] which subtracts a linear ramp function from the original waveform. The latter procedure works

well with the frequency increment used by the FFT, i.e., $m\omega_o$, where m equals an integer, ω_o equals $1/(2\pi T_N)$, and T_N equals the time window of the oscilloscope trace; but the procedure is awkward for the DFT when ω is not equal to ω_o. (3) the Gans Windowing procedure[29,75] which is

$$F_{WA}(t) = f(t) \quad \text{for } o \leq t < T_N$$

$$F_{WA}(t) = -f(t - T_N) + f(o) + f(T_N) \quad \text{for } T_N \leq t < 2T_N \qquad \text{II-11}$$

where $F_{WA}(t)$ equals the final waveform to be transformed, f(t) equals the original waveform, and f(o) equals f(t) at the first point. (Equations 4-11 are from reference 71, page 5-16.)

(4) An Extended Cosine Bell:[71]

$$W = 0.5(1 - \cos(2\pi 5t/T)) \quad \text{for } t = 0 \text{ to } T/10 \text{ and } t = 9T/10 \text{ to } T, \qquad W = 1 \quad \text{for } t = T/10 \text{ to } 9T/10 \qquad \text{II-12}$$

(5) A half cycle sine:[71]

$$W = \sin \pi t/T \quad \text{for } t = 0 \text{ to } T, \qquad \text{II-13}$$

(6) A triangle:[71]

$$W = 2t/T \quad \text{for } t = 0 \text{ to } T/2$$
$$W = -2t/T + 2 \quad \text{for } T/2 \text{ to } T \qquad \text{II-14}$$

(7) A Hamming Cosine:[71]

$$W = 0.5(1 - \cos 2\pi t/T), \quad \text{for } t = 0 \text{ to } T \qquad \text{II-15}$$

(8) A Half cycle (sine)^3:[71]

$$W = \sin^3(\pi t/T), \quad \text{for } t = 0 \text{ to } T \qquad \text{II-16}$$

(9) A Hamming:[71]

$$W = 0.08 + 0.46(1 - \cos 2\pi t/T), \quad \text{for } t = 0 \text{ to } T \qquad \text{II-17}$$

(10) A (Cosine)^2:[71]

$$W = [0.5(1 - \cos 2\pi t/T)]^2, \quad \text{for } t = 0 \text{ to } T \qquad \text{II-18}$$

(11) The Parzen equation:[71]

$$W = 1 - 6 \times (2t/T - 1)^2 + 6 \times (|2t/T - 1|)^3$$
$$\text{for } t - T/4 \text{ to } 3T/4$$

$$W = 2(1 - |2t/T - 1|)^3 \qquad \text{II-19}$$

for t = 0 to T/4 and
t = 3T/4 to T .

Procedures 4 - 11 are windowing functions, where T equals the time window on the oscilloscope and t equals the time of each point. The value of W is multiplied by the value of the original time domain data, thus forcing the original base line and last points of the time domain waveform to have approximately the same value.

The systems that gave the best results were the Samulon procedure, the Gans Windowing procedure, and a modified Extended Cosine Bell. Since a DFT was being used, the Gans Windowing procedure became less efficient because it consumed large amounts of computer time to complete a 1024 point transform. The Extended Cosine Bell was modified so that W multiplied only the end of the waveform instead of both ends, and so that the number of divisions the time window is divided into was chosen by the user of the program instead of the number of divisions being set to ten (see equation II-12). Unfortunately, the Extended Cosine Bell procedure adds lobes onto the simulated waveform. The program still needs modification to produce accurate simulations from reference waveforms that have large leakage error. If the frequencies used to calculate ε^* of the simulated sample can be matched to the frequencies of an FFT routine, then the simulation can be rapidly accomplished. The Gans procedure would, thus, not be time prohibitive in this circumstance.

CHAPTER III
RESULTS AND DISCUSSION

Introduction

Previously, this group has used TDR to study mixed-valence complexes such as Eu_3S_4 and $La_{1-x}Sr_xMO_3$, where M is equal to Co, Mn, Fe, and Ni; where x equals 0.1 for all M's; and x is equal to 0.1, 0.2 and 0.3 when M equals Fe.[31,32] The samples were acquired and analyzed in the time domain with equations derived by Cole[51]

$$\epsilon(t) = \epsilon_\infty + (\epsilon_s - \epsilon_\infty)(1 - e^{-t/\tau}) \qquad \text{I-36a}$$

$$\Phi(t) = \epsilon_\infty + (\epsilon_s - \epsilon_\infty)(1 - \exp(-(t - \frac{Tr}{2})/\tau) + \frac{C_s}{lC_c} =$$

$$\frac{c}{l}\int_0^t \frac{P(t')}{2V_0}\,dt' + \frac{c}{l}\int_0^t \frac{P(t')\,P(t-t')}{4V_0^2}\,dt' +$$

$$(\frac{c}{l})(\frac{TrP(Tr)P(t)}{8V_0^2}) \text{ for } t > T_R\ , \qquad \text{III-1}$$

where C_s equals the stray-end capacitance of the sample cell, C_c equals the coaxial-line geometric capacitance per unit length, l equals the measured depth of the sample in the sample cell, c equals the speed of light, and P(t) equals V_0 - R(t). In these equations, V_0 is the incident pulse as it passes the sampler, and R(t) is the reflections from the sample cell containing the sample (see Chapter I). It is assumed that, since C_s is small, the term

C_s/C_c is negligible in equation III-1. The Tau for the process is evaluated by the Guggenheim's method (see below).[1,2,31,32] If the dipolar relaxation process has only one mode of relaxation, then a plot of $\ln[\ \Delta\Phi(t)\ ]$ versus time yields a straight line with the slope equal to $-1/\tau$, where $\Delta\Phi(t)$ equals $\Phi(t + \Delta n) - \Phi(t)$ and Δn equals an arbitrary constant. Both Eu_3S_4 and $La_{1-x}Sr_xFeO_3$ showed only one mixed-valence relaxation process leading to Guggenheim plots with straight-line segments except, as Bunker states (reference 1, page 134), "at short times where rise time effects apparently interfere with the data collection." The $La_{1-x}Sr_xFeO_3$ sample also had dc conductivity through the sample in addition to the dipolar relaxation due to electron transfer between adjacent Fe^{III}/Fe^{IV} sites. In contradiction to the work of Bunker and Kroeger,[1,2,31,32] Doan and the author have found that the latter perovskites have more than one relaxation process. The differences between the two sets of results are caused by the latter set being obtained by the Fourier Transform analysis instead of the Time Domain analysis used by Kroeger and Bunker.[1,2,31,32] Thus, equation III-1 does not accurately describe the relaxation processes in the $La_{1-x}Sr_xFeO_3$ systems.

The time domain analysis has several associated problems which have been corrected or improved in this work. A summary of the major changes are given below. The time domain analysis does not completely account for (1) propagation effects in the sample or coaxial line; for (2) the fact that the total voltage in the coaxial line equals V(t) which equals $V_o(t) + R(t)$ instead of

$V_o(t)$; or (3) for the fact that $V_o(t)$ and R(t) have a finite risetime and amplitude. These problems were corrected by switching to the Fourier Transform analysis where the propagation correction factor, f(Z), and the ratio of DIFF(t)/SUM(t) could be used. (See equation I-70 through I-73.) The ratio gives an exact account of the total voltage in the coaxial line and removes symmetrical response functions of the equipment, g(s), from the response function of the sample, i.e.,

$$R(s) = \frac{g(s) * DIFF(s)}{g(s) * SUM(s)} , \qquad \text{III-2}$$

where DIFF(s) and SUM(s) are the algebraic differentiation and summation of the sample response functions before convolution with g(s), R(s) equals the ratio DIFF(s)/SUM(s), and * implies convolution. The symmetrical instrumental response function, g(s), cancels out in the ratio given in equation III-2. The asymmetrical response function of the equipment as well as joint reflections from the equipment, can be accounted for by use of the bilinear equation (see equation I-92). The latter correction factor can not be applied to the time domain analysis previously carried out within the group.

With the presently used single-channel TDR equipment (see below), the error in time referencing of the sample and reference is usually equal to or less than one address. The error is caused by a horizontal drift on the oscilloscope display which does not equal an integral number of $n\Delta t$, where Δt equals the time

window/(P/W). In previous work, the origins of the reference and sample were determined graphically. The intersection of the slopes from the base line and the first reflection, R1 in Figure I-9, from the sample cell was assigned to origin (t equals 0) (see Figure 7 in reference 2). This system is prone to larger errors in time referencing than the present system. Also the sample depth was a measured depth (l in equation III-1) which had to be experimentally determined for each sample. The error in each measurement of sample depth can be as large as 10%. In the present system, the sample cell will have a constant effective sample depth, d, with all samples that have a depth greater than the critical depth of each sample cell. Also in this study, all of the time domain points, e.g., 1024 points, were used to analyze the relaxation processes. In previous time domain analysis where the values of each point were obtained graphically, only a few selected points were used in the analysis. The present system, thus, has better time domain resolution.

The equipment presently being used is an improvement over earlier equipment. The oscilloscope and its modules are more stable, e.g., they have less drift, and have faster rise times than the previous equipment. The oscilloscipe also has the ability to signal-average the waveforms as they are being acquired. The S/N enhancement is less than $\sqrt{N}$, however, where N equals the number of averages, because the algorithm used by the digitizing oscilloscope does not weight all points and separate waveforms equally. Over the frequency range being studied, the Gore coaxial

cables are low-loss cables, which are necessary for obtaining good data. As mentioned above, the sample cells presently being used have a constant sample depth in contrast to earlier cells in which the sample depth was measured with calipers for each solid sample.

To obtain reasonable results from the data acquired with the improved equipment, one also needs computers that perform well. All DFT, Discrete Fourier Transform, calculations must be carried out on the VAX computer in double precision. The IBM CS-9000 computer has a memory management problem associated with double precision calculations and, therefore, double precision DFT calculations cannot be done on the IBM CS-9000 computer presently in use. The single precision DFT results on either computer for the higher frequencies, e.g., for frequencies above 1 GHz, are noticeably different from the double precision results.

The present equipment and programs have been tested with methanol, ethanol, propanol, and butanol and yield results for τ, ε_∞, and ε_S which are comparable with values found in the literature.[41,42,54,70,71] The fit of the experimental data to the dispersion plot, e.g., to the Cole - Cole plots, for each of the above alcohol standards was improved when the bilinear correction factor was applied.

The results become more complicated when the liquid samples, i.e., the above alcohols, acetone, DMA, diethyl ether, benzene, and water, are replaced with dipolar relaxing solid samples. (The $La_{1-x}Sr_xFeO_3$ samples are discussed in detail by Doan.[30]) The lower

Sr^{3+} dopant level ($x \leq 0.1$) samples show relaxation(s) that can be described by the circular arc formulism (see equations I-54 → I-57). The $[Fe_3(O)(Ac)_6X_3]$ • solvent samples, where X equals H_2O or C_5H_5N, and Ac equals acetate ion, show smooth curvature in the DISPA only at low frequencies.

The structure of $[Fe_3(O)(Ac)_6(H_2O)_3]$ is shown in Figure III-1. The three irons and the μ_3 - O group are coplanar.

DIFF(t) And ε' Versus ln (Frequency) Results

Selected difference curves (DIFF(t) equals the Reference (t) - Sample (t), for X equals H_2O and time window equals 5 nsec) are shown in Figure III-2. The area under the DIFF(t) as $t \to \infty$ (also called P(t)) is proportional to ε_S of the sample. A representative sample voltage reflection curve in a 2 nsec time window of $[Fe_3(O)(Ac)_6(H_2O)_3] \cdot H_2O$ is given in Figure III-3. In this figure, the voltage rises rapidly from the initial base line value to its maximum value, and the initial dip resulting from the first reflection from the sample cell is small. This type of behavior may indicate that τ for the dipolar relaxation is short and ε_∞ is small. (See below for a further discussion of these effects.) The rapid rise of the voltage curve in Figure III-3 manifests itself in the rapid fall of the DIFF(t) curve in Figure III-2.

The peak height and width of the DIFF(t) curves for the above sample generally increases with increasing sample temperatures. The DIFF(t) curves at the temperatures of 233, 253, 273 K were almost identical. However, the pyridine adduct had quite different

Figure III-1. Structure of $[Fe_3(O)(Ac)_6(H_2O)_3]$.[76] The three irons and the bridging oxygen atom are coplanar.

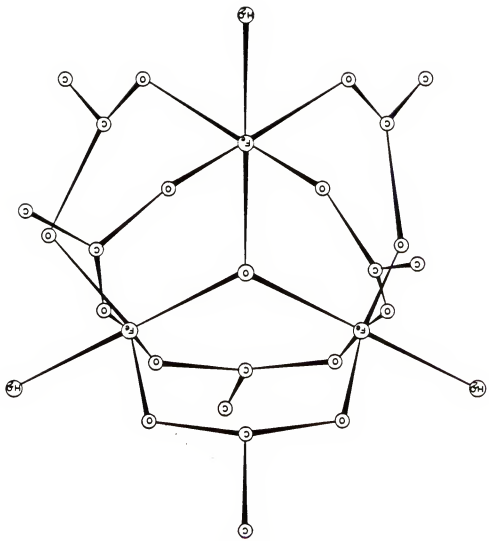


Figure III-2. DIFF(t) graphs for $[Fe_3(O)(Ac)_6(H_2O)_3] \cdot H_2O$ at temperatures 188 K (smallest peak), 230 K, and 298 K (largest peak). The peak height and width increase as temperature is increased. Also notice that there is non-random noise in the baseline of the three curves.

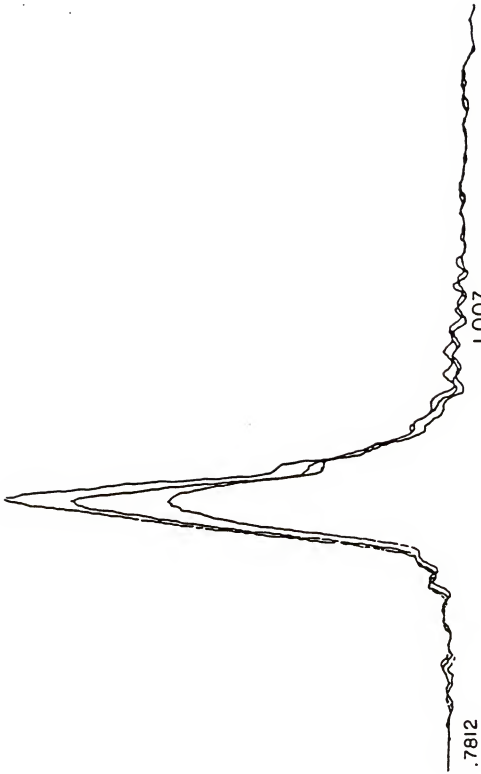

.7812
1.007

Figure III-3. A voltage versus time display from the oscilloscope of $[Fe_3(O)(Ac)_6(H_2O)_3] \cdot H_2O$ at 199 K. Notice that the figure rapidly rises from its base line value to its maximum value and that there is only a small initial dip resulting from the first reflection from the sample cell.

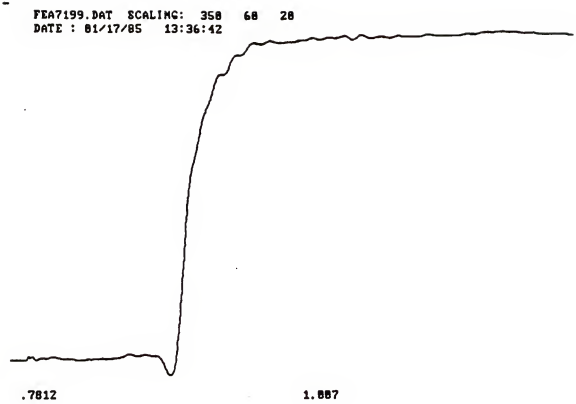

FEA7199.DAT SCALING: 358 68 28
DATE : 01/17/85 13:36:42
.7812
1.887

Figure III-4. The graph of ε' versus ln (frequency) for $[Fe_3(O)(Ac)_6(H_2O)_3] \cdot H_2O$ at 298 K in a 5 nsec time window. Notice how small the change in ε' is. Compare the magnitude of this $\Delta\varepsilon$, which equals $\varepsilon_s - \varepsilon_\infty$, with that of n-propanol in Figure I-19.

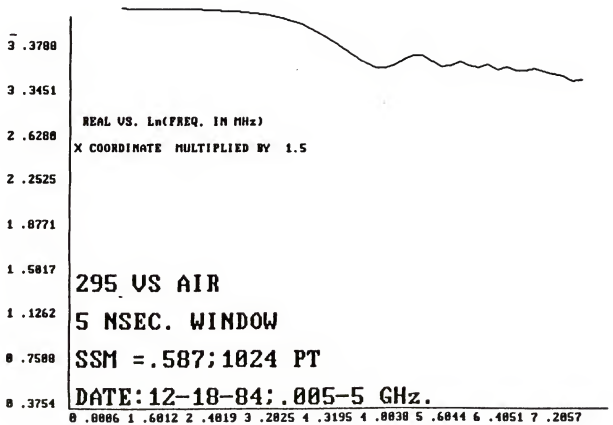
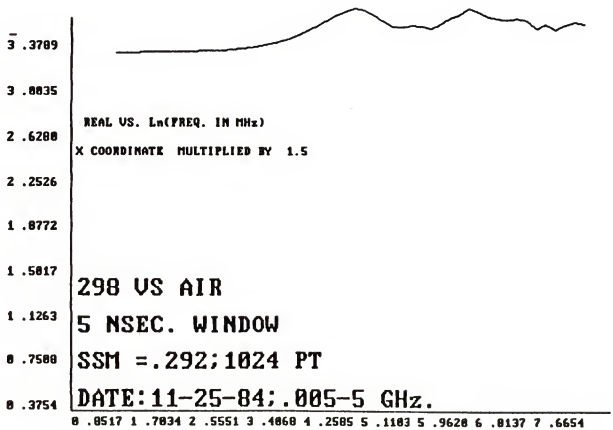

3 .3788
3 .3451
2 .6288
2 .2525
1 .8771
1 .5017
1 .1262
0 .7508
0 .3754
REAL VS. Ln(FREQ. IN MHz)
X COORDINATE MULTIPLIED BY 1.5
295 VS AIR
5 NSEC. WINDOW
SSM =.587;1024 PT
DATE:12-18-84;.005-5 GHz.
0 .0006 1 .6012 2 .4019 3 .2825 4 .3195 4 .0030 5 .6044 6 .4051 7 .2057

Figure III-5. The graph of ϵ' versus ln (frequency) for $[Fe_3(O)(Ac)_6py_3] \cdot x\ py \cdot z\ H_2O$, where the complex has pyridine, py, and water in its lattice, at 298 K in a 5 nsec time window. In this figure, there is a rise in the measured ϵ' value. Notice that the value of ϵ' increases with ln (frequency). This trend is opposite that of the predicted behavior for a Debye dielectric sample. See Figure I-7 for comparison with theoretical curves.


3 .3709
3 .0835
2 .6288
2 .2526
1 .8772
1 .5017
1 .1263
0 .7508
0 .3754
REAL VS. Ln(FREQ. IN MHz)
X COORDINATE MULTIPLIED BY 1.5
298 VS AIR
5 NSEC. WINDOW
SSM =.292;1024 PT
DATE:11-25-84;.005-5 GHz.
0 .0517 1 .7034 2 .5551 3 .4068 4 .2585 5 .1103 5 .9620 6 .8137 7 .6654

results from the above. The DIFF(t) curves at 184 and 193 K are almost identical, yet, from 203 through 243 K the peak height and area decrease with increasing temperature, then increase again from 263 to 295 K. The peak height and area of the 295 K sample was larger than the 184 K sample. Figures III-4 and III-5 graph ε' versus ln (frequency), where the measured frequency was in MHz, for x equals H_2O and C_5H_5N, respectively, at room temperature and in a 5 nsec time window. The former shows the theoretically-predicted trend of ε' with ln (frequency) for a sample exhibiting dielectric relaxation, i.e., ε' decreases as the value of ln (frequency) increases. The latter shows the opposite trend of ε' as a function of ln (frequency). (See Figure I-7 for comparison with the theoretical curves for samples showing Debye dielectric relaxation.) At all temperatures studied, the shape of the ε' versus ln (frequency) curve looked like Figure III-4 for the water adduct of the iron trimer. On the other hand, at low temperatures for the X equals C_5H_5N sample, the graph appeared as it does in Figure III-4 with a hump growing in, as seen in Figure III-5, when the temperature is raised. Also the $\Delta\varepsilon$, which equals $\varepsilon_s - \varepsilon_\infty$, is small for both samples. This $\Delta\varepsilon$ value is the measured value. Since air is in the sample, the measured ε_s and ε_∞ are less than the real ε_s and ε_∞ of the sample. If the density of the powder used and that of the bulk material are known, then the true ε_∞ and ε_o can be estimated by multiplying the measured values by the ratio of the densities.[2]

ϵ'' Versus ln (Frequency) Results

Figures III-6 and III-7 show graphs of ϵ'' versus ln (frequency) for X equals H_2O at 166 K and 295 K in a 5 nsec time window. At the lower temperatures, the ϵ'' versus ln (frequency) curve approximates the theoretically predicted trend of ϵ'' increasing to its maximum value then decreasing back towards the base line value. (See Figure I-7 for comparison to an idealized ϵ'' versus ln (frequency) curve.) In contrast, as the temperature was raised, the higher frequency portion of the ϵ'' curve did not return to the base line as did the low temperature samples. The distortion of the higher frequency values of ϵ'' increased as the temperature was raised. The pyridine adduct followed the same general trend of increased distortion of ϵ'' as the temperature was raised.

In the 2 nsec time window, the behavior of ϵ'' as a function of ln (frequency) for the aqua complex at the higher temperatures, e.g., room temperature, was different from that of the same complex in the 5 nsec time window. The tendency of ϵ'' to increase to its maximum value as ln (frequency) is increased was the same as it in the 5 nsec time window. By contrast, the higher frequency portion of ϵ'' did not return toward the base line but formed a plateau, i.e., the ϵ'' versus ln (frequency) appeared as a flattened "S" shaped curve.

This distortion of the higher frequency ϵ'' data from the theoretically predicted shape in the 2 or 5 nsec time window is likely caused by three factors: 1. that the Signal/Noise ratio was

Figure III-6. The graph of ε'' versus ln (frequency) for $[Fe_3(O)(Ac)_6(H_2O)_3] \cdot H_2O$ in a 5 nsec time window at 166 K. Compare this sample with n-propanol in Figure I-20. The general shapes of the two figures are the same, yet the higher frequency portion of Figure III-6 shows more distortion from the idealized behavior of a relaxing Debye dielectric sample than does Figure I-20.

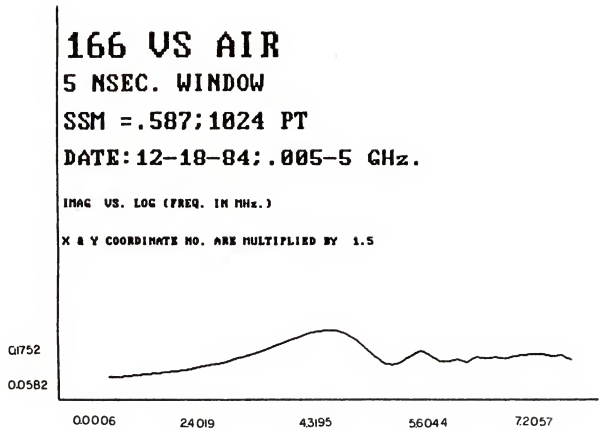
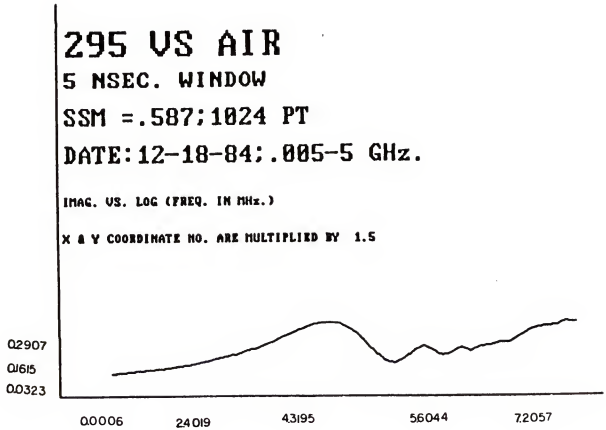

166 VS AIR
5 NSEC. WINDOW
SSM =.587;1024 PT
DATE:12-18-84;.005-5 GHz.
IMAG VS. LOG (FREQ. IN MHz.)
X & Y COORDINATE NO. ARE MULTIPLIED BY 1.5
0.1752
0.0582
0.0006
24019
43195
56044
72057

Figure III-7. This is the same compound as in Figure III-6 except that the temperature of this sample is 298 K. The high frequency data has an extra rise.


295 VS AIR
5 NSEC. WINDOW
SSM =.587;1024 PT
DATE:12-18-84;.005-5 GHz.
IMAG. VS. LOG (FREQ. IN MHz.)
X & Y COORDINATE NO. ARE MULTIPLIED BY 1.5
0.2907
0.1615
0.0323
0.0006
2.4019
4.3195
5.6044
7.2057

too small, and, accurate data was, therefore, not obtainable; 2. that there were overlapping dielectric relaxation processes with significantly different Tau's; and 3. that the sample cell (a capacitor) responded as an RLC circuit (resistance, inductance, and capacitance) instead of an RC circuit (resistance and capacitance). The sample cell ideally responds as a linear RC circuit when it is filled with a non-conductive Debye dielectric sample (see equations I-31 and I-32). The charging current of the capacitor may become non-linear at the higher frequencies when the sample cell responds as an RLC circuit. The circuit shall be defined in this text as "non-well-behaved" when the circuit becomes non-linear.

The second factor, overlapping dipolar relaxation processes, is unlikely. The magnitude of the distortion of the higher frequency data in the ε" versus ln (frequency) curve increases sizably with increasing temperature, yet the ε' versus ln (frequency) shows little change with temperature for the aqua adduct. A larger change in the ε' curve would have been expected for such large changes in the magnitude of ε" if overlapping dipolar relaxation processes were the cause of the rise in the higher frequency ε" values as the temperature was increased.

The differences between the sample and the reference time domain waveforms became increasingly minute as ε_∞ and $\Delta\varepsilon$ decreased in magnitude. If in addition τ is also short, the difference of the voltage reflections from the sample and the reference may well be buried in the noise. The error resulting from random noise and

the error resulting from drift, e.g., in the risetime or in the horizontal position of a time domain point, in the TDR equipment must, therefore, be quite small for the accurate detection of the differences between the time domain waveforms of the sample and reference when ε_∞ and $\Delta\varepsilon$ are small and τ is short. The random noise in the present TDR equipment is minimized by signal averaging the time domain (1024 points) data 150 times. Improvements in the S/N ratio are still needed for the $[Fe_3(O)(Ac)_6X_3] \cdot y$ solvate complexes for which the measured $\Delta\varepsilon$ is small, i.e., those with values ranging from 0.7 to 2. The problems caused by noise will decrease if new sample cells can be designed that increase the signal strength from the sample cell. The S/N ratio will be increased by new cells which cause the voltage pulse to interact more with the sample. Also, the use of dual channel TDR or the difference method of TDR,[37,54,55] may help to minimize the error caused by noise. These three items, i.e., new sample cells, dual channel TDR, and the difference method of TDR, will be discussed further below.

The third factor which may cause the distortion of the higher frequency portion of ε'', i.e., the sample cell responding as an RLC circuit, will be briefly discussed later in this chapter. (For good applications of circuit analysis and electronics to chemistry, see references 77 and 78.)

To briefly summarize, the distortion of the higher frequency data of the ε'' versus ln (frequency) curve may be caused by three factors. The first and third factors, i.e., the excessivley small S/N ratio and the RLC response of the sample cell are likely the

major causes of the distortion. The second factor, the overlapping dipolar relaxation processes, is unlikely a major cause of the distortion because the ε' versus ln (frequency) data show only a small change over the same temperature range at which the ε'' data become distorted.

ε' Versus (ε'' x Frequency) Results

As mentioned earlier, τ or f_c can be derived by plotting ε' versus (ε'' x frequency), i.e. f_c equals $^{-1}$/slope[42]. Each dipolar relaxation process should produce a straight line segment if the differences in their Tau's are large enough. Figure III-8 - III-13 show examples of this technique for two different sets of acquisitions of the water adduct of the iron trimer. Figures III-8 - III-10 demonstrate samples that were acquired in a 5 nsec time window. There is a general trend demonstrated in the figures for the slope of the second line segment (the higher frequency data portion) tend to become more positive as the temperature is increased. In fact, for the temperatures between 206 and 266 K, the slope of the second line segments are positive. This trend is reversed by the room temperature sample, which gave a negative slope as did the low temperature samples (see below).

If electron transfer between the iron sites of the iron trimer is the only source of dipolar relaxation, and if the sample cell performs as a linear RC circuit, then a positive slope of the ε' versus (ε'' x frequency) graph is not possible. Unfortunately, if the sample cell responds as an RLC circuit, then, at some critical frequency determined by the circuit, the slope of the ε' versus (ε''

Figure III-8. The graph of ε' versus (ε'' x frequency) for $[Fe_3(O)(Ac)_6(H_2O)_3] \cdot H_2O$ in a 5 nsec time window at 166 K. Compare this figure with Figures III-9 and III-10. The graph of the low temperature sample (166 K) has two distinct line segments, both of which have negative slopes. The second line segment, the higher frequency data, of the 206 K sample (Figure III-9), has a positive slope, while the higher frequency data of the 298 K sample has a slightly negative slope.

Ideally, for a Debye dielectric sample, the positive slope of the line segments cannot be positive because the τ's for the relaxation processes must have positive values and because f_c equals $1/(2\ \pi\tau)$ and f_c equals -1/(slope of the line segment).

REAL VS. IMAG. * FREQ. IN CHn.
X COORDINATE MULTIPLIED BY 2.5
Z̄ .3337
1 .8151
1 .2965
0 .7779
0 .2593
0 .60 0 .17 0 .29 0 .40 0 .52

Figure III-9. The same sample as Figure III-8 except that the sample is at 206 K.

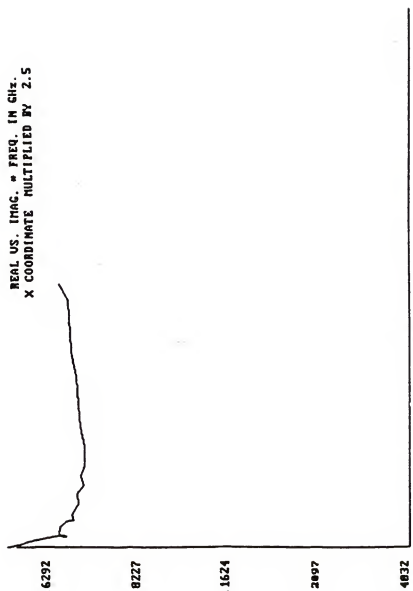

REAL VS. IMAG. = FREQ. IN GHz.
X COORDINATE MULTIPLIED BY 2.5
3 .6292
2 .8227
2 .1624
1 .2897
0 .4832
0 .117 0 .352 0 .587 0 .822 1 .571

Figure III-10. The same sample as in Figure III-9 except that the sample is at 298 K.

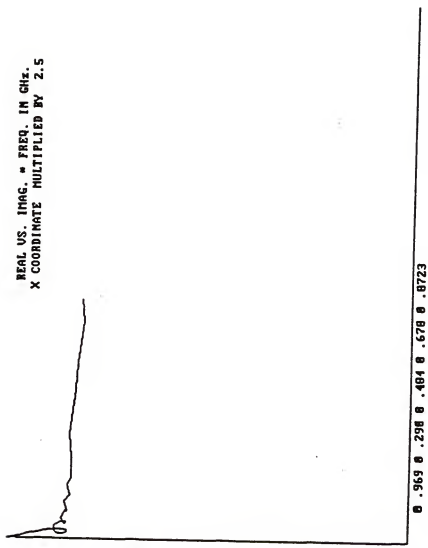

REAL VS. IMAG. * FREQ. IN GHz.
X COORDINATE MULTIPLIED BY 2.5
3 .3708
2 .6288
1 .8771
1 .1262
0 .3754
0 .969 0 .298 0 .484 0 .670 0 .8723

Figure III-11. The same compound as in Figure III-8 except that the time window is 2 nsec instead of 5 nsec and that the sample is packed tighter in this series. The sample is at 166 K. Notice, in contrast to Figure III-8 - III-10, that the higher frequency data has a negative curvature that straightens out as the temperature is increased. See Figure III-12 and III-13 for the 246 and 298 K samples in the 2 nsec time windows.

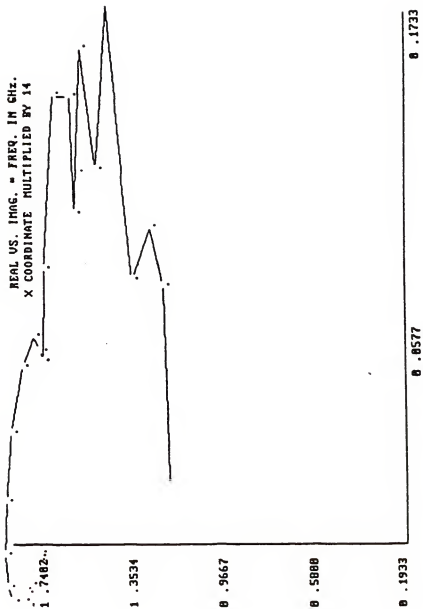

REAL VS. IMAG. - FREQ. IN GHz.
X COORDINATE MULTIPLIED BY 14
1 .7482
1 .3534
0 .9667
0 .5800
0 .1933
0 .8577
0 .1733

Figure III-12. The same sample as Figure III-11 except that the temperature is 246 K.

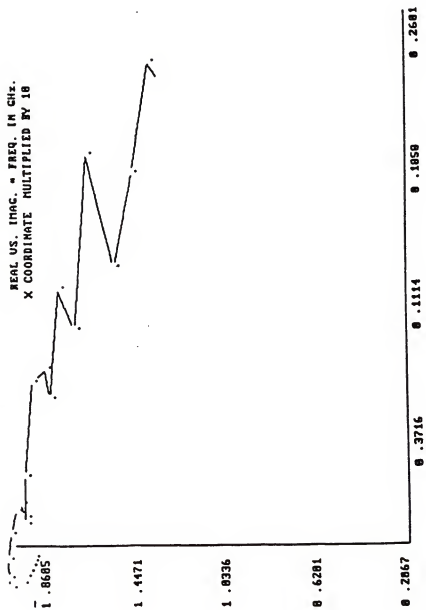
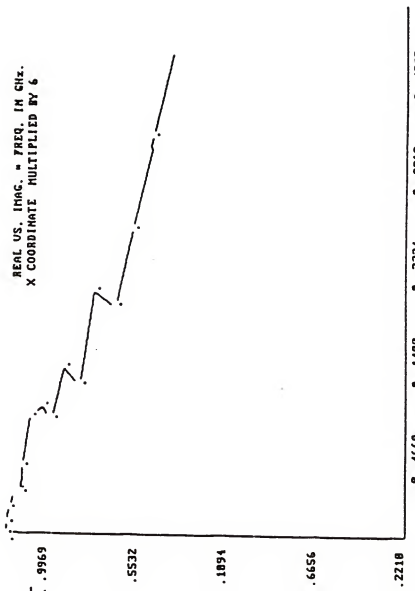

REAL VS. IMAG. + FREQ. IN GHz.
X COORDINATE MULTIPLIED BY 10
1 .8685
1 .4471
1 .0336
0 .6201
0 .2067
0 .3716
0 .1114
0 .1859
0 .2681

Figure III-13. The same sample as in Figure III-11 except that the temperature is 298 K.


REAL VS. IMAG. = FREQ. IN GHz.
X COORDINATE MULTIPLIED BY 6
1 .9969
1 .5532
1 .1094
0 .6656
0 .2218
0 .4669
0 .1408
0 .2331
0 .3268
0 .4202

x frequency) graph may become positive.[56] A possible explanation of the negative slope of the room temperature sample is that the relative magnitude of the error (which is caused by the sample cell not responding as an ideal RC circuit) decreases as the temperature is raised in comparison to the magnitude of the detected dipolar relaxation. At all temperatures, the low frequency line segments of the ε' versus (ε'' x frequency) graphs have approximately the same slope and, thus, the same f_c value, i.e., approximately 120 ± 4 MHz. The values of τ for the three samples with negative slopes are given in Table 2.

Figures III-11 - III-13 are of the same sample as above except that the time window was 2 nsec instead of 5 and the sample cell was removed from the coaxial line before packing. The time domain data were better resolved in the 2 nsec than in the 5 nsec time window since there was necessarily less time between each time domain point in the former. Also, the sample in the 2 nsec time window was packed tighter because the sample cell was removed from the coaxial line before it was packed. Figure III-11 - III-13 demonstrate that the negative curvature of the graph at higher frequencies straightened out as the temperature increased. Different time windows and different packings of the sample cell may have been the cause of the differences between the 2 and 5 nsec time windows. It should be noted that, in both cases [Figure III-8 - III-10 and Figures III-11 - III-13, (5 and 2 nsec time windows, respectively)] the slopes of the higher frequency components tended to become more positive.

The pyridine adducts have ε' versus (ε'' x frequency) graphs

Table 2

Tau Values for $[Fe_3(O)(Ac)_6(H_2O)_3] \cdot Z\ H_2O$.

Mössbauer[a]		5 nsec[b]		2 nsec[b]	
T(K)	τ[c]	T(K)	τ[c,d]	T(K)	τ[c,d,e]
130	196				
170	116	166	0.14		
		186	0.14	188	0.25
200	95.3	206	-[f]	206	0.32
225	21.5	226	-[f]		
235	22.0			230	0.26
245	20.4	246	-[f]		
260	18.0	266	2.8	266	0.34
298	2.5	298	2.6	298	0.30

a. Reference 62 $[Fe_3(O)(Ac)_6(H_2O)_3]$, z = 0

b. $[Fe_3(O)(Ac)_6(H_2O)_3] \cdot H\ O_2$, z = 1

c. in nanoseconds

d. τ from TDR, τ_{TDR}, converted to τ from Mössbauer, τ_{Moss}, by the equation $2\tau_{TDR} = \tau_{Moss}$

e. The 2 nsec time window is extended by 4 nsec of zero filling (2048 points).

f. The slopes of the graphs are positive.

that are nearly linear over most of the frequency range studied, 0.005 - 5 GHz. The small $\Delta\varepsilon$ and ε_∞ of this sample produced such a small change on the present single channel equipment that the τ's obtained from it should be interpreted to indicate only a general trend. The f_c data (f_c equals $1/(2\ \pi\tau)$), which was derived at selected temperatures and from the approximate frequency range of 1.6 to 2.8 GHz region of the ε' versus (ε'' x frequency) graphs, are (113 K) f_c = 5.5 GHz, (213 K) f_c = 7.7 GHz, and (298 K) f_c = 40.5 GHz. The last critical frequency, f_c, is obviously well beyond the maximum frequency limit of the TDR equipment. This large value of f_c may imply that the rate of electron transfer is outside the time scale of the equipment and/or that the slope of all or any of the line segments used to obtain τ are made more positive by the sample cell responding as an RLC circuit.

Samples with larger values of ε_∞ and $\Delta\varepsilon$ and longer τ's than the iron trimer mentioned above should have a larger S/N ratio than the iron trimers, assuming that the samples with the larger ε_∞, etc., have at least the same number of charge carriers per sample as the iron trimers. They should therefore yield better results than the iron trimers did as long as the sample cell responds as a "well - behaved" circuit. An example of this situation is given below.

Analysis of the $La_{1-x}Sr_xFeO_3$ data demonstrated that the low dopant levels (e.g. x equals 0.010) produced "well behaved" Cole-Cole plots and ε' versus (ε'' x frequency) plots. At higher dopant levels (e.g. x equals 0.2) the graphs of ε' versus (ε'' x frequency) had a "saw-tooth" structure with negative curvature. This

structure and curvature may be at least partially explained by the higher dopant levels, which caused (1) a change in the R, L, and C components of the sample and cell, and (2) a structural change in the perovskite. The latter change may cause ε_s and ε_∞ to vary. These structural changes may allow for more pathways of electron transfer within and through the lattice, thus, creating the possibility of many overlapping relaxation processes interacting with applied fields which may cause the graph to curve. If the relaxation processes do not independently interact with the applied field, an under-dampened RLC circuit may be produced.[58] The sample cell thus could cause the negative curvature seen in the ε' versus (ε'' x frequency) graph of the higher dopant level perovskites, as well as in the iron trimer samples.

General Discussion

The results of the variable temperature TDR experiments described above and elsewhere can be used to obtain the energy of activation, E_a, for the electron transfer between the adjacent metals sites, e.g., Fe^{III} - O - Fe^{IV}, in the mixed-valence compounds or a bulk transfer of electron through the solid, i.e., conduction

$$\tau = \tau_0 \exp[E_{th}/kT], \qquad \text{III-3}$$

$$\sigma = \sigma_0 \exp[-E_{th}'/kT], \qquad \text{III-4}$$

where τ_0 and σ_0 are the pre-exponential factors, k is the Boltzman constant, T is the temperature in Kelvin, E_{th}, the E_a of the

dipolar relaxation process, and E_{th}', the E_a for the conduction process. The two energies of activation, E_{th} and E_{th}', need not be the same unless they are for the same process. The relaxation times obtained from TDR are for dielectric relaxation processes only. The rate, k (see equation I-3), of electron transfer between the two metal sites in a mixed valence compound is

$$k = \frac{1}{2\tau_{TDR}}, \text{ or } k = \pi f_c, \qquad \text{III-5}$$

since

$$\tau_{TDR} = \frac{1}{2\pi f_c}, \qquad \text{III-6}$$

where τ_{TDR} equals τ of the dielectric relaxation process. It is important to note that, in most other techniques used to measure the rate of electron transfer, e.g., Mössbauer, the following relation exists

$$k = 1/\tau_{other}, \qquad \text{III-7}$$

where τ_{other} is the τ for the electron transfer process; therefore, $2\tau_{TDR}$ equals τ_{other}.

The rate of electron transfer in the complexes $[Fe_3(O)(Ac)_6 X_3] \cdot y$ solvate, where X equals C_5H_5N or H_2O, has been previously studied by Mössbauer and TDR. The results vary. Doan and Bunker[1,79] saw little to no relaxation of the water adduct species with the room-temperature TDR. Bunker states (reference 1,

page 178) that the relaxation process of the iron trimer:

> is not detected in the TDR, [because] the density of mobile electrons in the sample is not high enough to produce dielectric constants which are large enough to give rise to a well defined relaxation spectrum.

This statement is another way of saying that if $\Delta\varepsilon_{(measured)}$ (which equals $\varepsilon_{\infty(measured)} - \varepsilon_{s(measured)}$, and where (measured) is added to the symbols to re-emphasize that the measured value does not have to equal the actual value of these quantities) is small, then it will be difficult to characterize the relaxation process by TDR. C. Dziobkowski, et al[62] calculated relaxation times for the aqua adduct by Mössbauer (see Table 2). Also in Table 2 are the TDR results from the two different time windows, both of which are very different. The compound tested in Dziobkowski's experiment and in this work are different, i.e., there is H_2O in the lattice of the sample in this work.

Recently, Hendrickson, et al[80] found that $[Fe_3(O)(Ac)_6(py)_3]$, where py equals C_5H_5N and Ac equals CH_3COO^-, shows no increase in the electron transfer rate from ~ 100 to 315 K. The same complex with pyridine or benzene in the crystal lattice shows a temperature-dependent electron transfer-rate over the same temperature range. The same research also demonstrated that the three irons of $[Fe_3(O)(Ac)_6(4 - Etpy)_3](4 - Etpy)$, where 4 - Etpy equals 4-ethyl-pyridine, form an isosceles triangle at 163 K, but approach an equilateral triangle by 298 K.[80]

This result is in contrast with the X ray work quoted by Cannon et al[81] on the compounds $[Fe_3(O)(Ac)_6py_3]$ and $[Fe_2^{III}M^{II}(O)(Ac)_6(py)_3]$, where M equals Mn, Co, and $[Cr_2^{III}Fe^{III}(O)(Ac)_6(py)_3]^+$. The X ray study indicates that all the metal centers are equivalent at room temperature and indicates that the pyridine adduct of each complex is either a Class III mixed-valence complex or that the sample contains randomly disordered Class II complexes.[81] The two results, Mössbauer and X ray, are, thus, not in contradiction, since the interpretations of the latter results are ambiguous.

Hendrickson et al[80] attribute their results to a solid phase change in the solvated complexes as the temperature is raised. They proposed that the ligands and/or the solvent molecules change from a more ordered state to a dynamically disordered state as the temperature is raised. This dynamic disordering could then symmetrize the environment around the complex.

One interpretation of Hendrickson's proposed mechanism is that the solvent molecule, e.g., pyridine, in the lattice has a polar group, e.g., the nitrogen end of pyridine, pointing at one of the iron centers. At low temperatues, the solvent group is nearly stationary and has, therefore, a nearly constant dipole moment applied to one of the iron centers that may lower or raise the energy of the potential energy well for that iron center. This would, therefore, make the iron trimers asymmetric (see Figure I-2). If the energy of the potential energy well is lowered enough by the above process, then the electron may become "trapped" in the unique potential energy well. As the temperature is raised, the solvent molecule will tend to vibrate more in the lattice. The net

dipole moment on the odd iron site will, therefore, be less. As this process continues, the three iron sites become more alike, and, at some temperature, the three sites will become identical. At this temperature, the molecule may change from a Class II to a Class III complex. If this hypothesis is correct, then one must be careful not to assume that the compound is only one type of mixed valence complex over all temperatures studied unless there are data to indicate that there is not solid phase changes as the temperature is varied.

In further support for the solid phase change proposal, Hendrickson et al have shown that the pyridine solvated molecule undergoes two solid phase transformations.[82] The first occurs at 110 K and follows a higher order phase change. The second is a first order phase transformation and occurs at 190 K.[82] The latter result is in accordance with the DIFF(t) data for the pyridine sample in this work. The area under the DIFF(t) curve is constant at 184 and 193 K. However, at 193 K, the area under the DIFF(t) curve begins to decrease as the temperature is increased. This trend reverses at 263 K, i.e., the area under the DIFF(t) curve starts to increase as the temperature of the sample is increased. As mentioned above, the area under the DIFF(t) curve $t \rightarrow \infty$ is proportional to ε_s. One explanation of the temperature and DIFF(t) data is that there are solid phase changes at approximately 190 and 263 K which cause the static dielectric constant to have more than one maximum or minimum value as a function of temperature. The former temperature matches the temperature at which Hendrickson et al found a heat capacity change in their iron trimer sample.[82]

The constant value of ε_s (whose value is proportional to the area under the DIFF(t) curve) for the water adduct of the trimer in the temperature region of 233 - 273 K may be the result of solid phase changes, such changes of the iron trimer may cause heat capacity changes in the sample. Within the above temperature region, the sample would take at least 1 hour to reach temperature equilibrium after a 20 °C increase in the temperature of the sample dewar. For temperatures outside the above temperature range, the sample would come to temperature equilibrium within 20 to 30 minutes. The differing amounts of time it takes for the samples to arrive at temperature equilibrium could, thus, be the result of a heat capacity change and, therefore, a solid phase change of the sample.

In summary, it is important to realize when there are solid phase changes in mixed-valence compound, as the mechanism for the mixed-valence electron transfer and its E_a may vary with each phase. The TDR results may, thus, vary if the rates of electron transfer vary with each solid phase change. The TDR sensitivity to each mechanism of electron transfer may also vary as $\Delta\varepsilon$ and ε_∞ increase or decrease with each solid phase change. Also, as is obvious from the above discussion, the mechanisms of and the factors controlling the rate of electron transfer in these compounds are not yet understood.

Factors That May Have Effected The TDR Results

The differences of the TDR results from the Mössbauer results may be caused by a combination of several chemical and/or

instrumental factors. The major reasons that the two techniques gave different results for the iron trimer samples was that the TDR sample cell responded as an RLC circuit and that the sample and reference waveforms of TDR were too similar; therefore, an accurate description of the dipolar relaxation process could not be obtained from the present TDR equipment. A more complete description of the factors affecting the TDR results is given below. Bunker and Kroeger give good discussions of problems associated with obtaining rate data from Mössbauer.[1,2]

The possible factors that may be affecting the TDR results are given below. The factors that affect the rates of electron transfer may influence both the TDR and the Mössbauer results. Yet the factors that cause the changes in electron transfer rates may manifest themselves differently in TDR and in Mössbauer. An example of this is given in item 1 below.

1. As mentioned above, there may be solid phase changes which introduce new electron transfer mechanisms and result in the TDR equipment having varying degrees of sensitivity for the sample at different temperatures. The rate of electron transfer may be increased or decreased by this solid phase change. If the rates of electron transfer stay within the time scale of the Mössbauer equipment, and the difference between the two rates is greater than the minimum resolution of the Mössbauer equipment, then the change in rate should be detected. TDR, however, may not detect the change in the electron transfer rate if the ε_∞ and $\Delta\varepsilon$ become too small (because of the solid phase changes) for the TDR instrument to detect any dipolar relaxation resulting from the electron moving

from one iron center to another.

2. Since there are three metal sites in the trimers, there are three ground state potential wells in which the electron may reside.[81,83] It has been proposed that, at low temperatures, the electron transfers between two distinct iron sites (pathway 1); yet as the temperature is raised, the electron is initially delocalized between two of the iron sites. It then transfers to the third (pathway 2).[83] This situation of localized electron transfer versus partially delocalized transfer (inner sphere effects) may combine with solid phase changes mentioned above (outer sphere effects) and lead to a temperature dependence of the electron transfer rate that is non-Arrehenius in nature. For example, it is possible that the measured rate may not change as the temperature is varied, since different mechanisms of electron transfer are continuously being added or removed from the molecule. The probability that this one phenomenon would cause the measured rates to maintain a constant value is obviously small. Yet, having several distinct electron transfer mechanisms may easily cause a variation of the measured electron transfer rate, which is not a smooth function of temperature.

If the electron transfer rate can be described by a summation of Arrehenius rate equations, then the total rate, k_T, is

$$k_T = A_1 \exp(-Ea_1/kT) + A_2 \exp(-Ea_2/kT) + \ldots, \qquad \text{III-8}$$

where A_1 is not equal to A_2 and Ea_1 is not equal to Ea_2 unless by coincidence. This equation may describe the situation when both

pathways 1 and 2 mentioned above are present. If there are solid phase changes as well, terms may be added to or removed from the equation III-8. The total rate is, thus, a weighted combination of all relaxation mechanisms present at any one temperature. From this equation and the discussion concerning it, one can see that k_T does not have to follow a simple Arrhenius rate law based on one relaxation mechanism.

3. Bunker[1] proposed that the aqua complex contains sizable quantities of the non-mixed valence salt. This sample does not relax on the TDR time scale. In an attempt to discount this error as a possible reason that my TDR results were not consistent with the Mössbauer results, the iron trimers were made several times. Each preparation of the trimers varied from the previous preparation, all of which included making the iron trimers from $FeCl_2 \cdot 2H_2O$ and $FeCl_2 \cdot \emptyset H_2O$ which had been prepared separately from new starting materials. The pyridine sample was made twice from different batches of the aqua complex. No matter which sample was used in the TDR experiment, the results were always similar. A large impurity of $[Fe_3(O)(Ac)_6(H_2O)_3]Cl$ was, thus, unlikely.

4. The iron trimers were distroyed by the temperature change. This situation is unlikely because either the pyridine or the water samples can be cycled from room temperature to 188 K and then back to room temperature, etc. This cycling was repeated two times without the DIFF(t) curves significantly changing from cycle to cycle.

5. The extra joint reflections cause ε'' to become a poorly behaved function. The bilinear correction factor was applied to correct

for this problem. The low frequency data was improved, e.g., the low frequency curl (see Figures III-11 - III-13) on the ε' versus (ε'' x frequency) was removed, but the higher frequency data was only slightly improved, e.g., the positive slope of the 5 nsec time window of ε' versus (ε'' x frequency) was not corrected (see Figures III-8 - III-13).

6. Another possible reason is that the curvature of the ε' versus (ε'' x frequency) graph resulted from timing errors. The slope of this graph can be forced to become positive or to curl back upon itself if timing errors are large enough. To test to see if timing errors were the cause of the problem, the following experiments were done. The reference and sample were initially aligned by the timing marker from the oscilloscope. The sample was then moved up to 10 addresses later in time, after which the reference waveform was moved up to 10 addresses earlier in time in reference to the original timing marker. Each of the numerous shiftings of the relative position of the sample to the reference at each temperature failed to correct the problem. The waveforms were also moved in non-integral numbers of address by using equation I-82. This source of error is thus not a major cause of the problems with ε''.

7. The rate of electron transfer is at all temperatures faster or slower than the equipment can follow. If the Mössbauer data (see Table 2) has any significance, this factor cannot be a cause of the poorly behaved ε'' data.

8. It is known that the non-mixed valence aqua adduct has magnetic coupling between the trimers.[62,85,86] The communication is

presumed to proceed by H-bonding between the trimers. It is, therefore, possible that there could also be communication between the mixed-valence clusters in which the electron transfer in one cluster would modify the rate of electron transfer in an adjacent cluster, e.g., it may weaken or strengthen a H-bond to a carbonyl group or to the μ_3 - O group. This communication could, thus, change the potential energy surfaces on which the electron travels when it is transferred. The molecules excited first by the voltage pulse in the TDR sample cell may, thus, have different relaxation times than the molecules which they influence. The likely outcome of this is a distribution of relaxation times instead of one. This situation may affect the data, but as mentioned above, it is unlikely that the TDR can detect several strong relaxation process competing in the higher frequency region. In addition, even if there were several strong dipolar relaxation processes present in the higher frequency region, the ε'' versus ln (frequency) graph would not likely show an oscillatory behavior.[58]

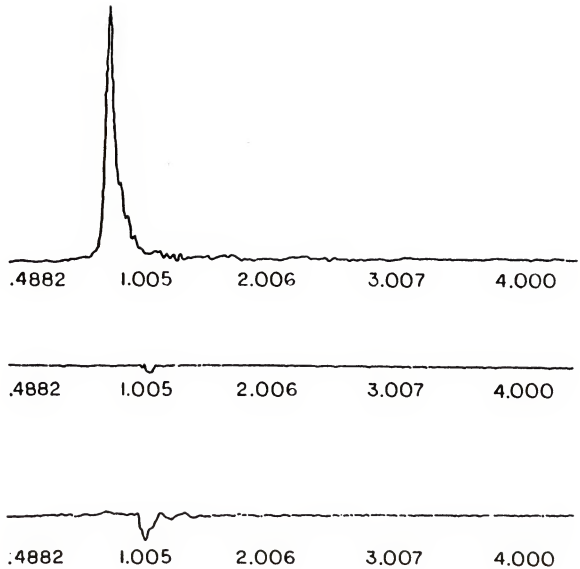
9. The techniques used to transform the time domain data into the frequency domain may also affect the TDR results. The DFT (Discrete Fourier Transform, see Chapter I) produces a relaxation at a frequency which is equal to 1/(time window) on the oscilloscope. This mathematically created relaxation can interfere with the interpretation of the electron transfer results. The time window should, thus, be at least 4 to 5 times larger than the Tau of the dipolar relaxation to ensure that the τ from the choice of time windows and the τ from the dipolar relaxation process do not overlap.[56] The possibility of this problem is eliminated by

mathematically extending the time window of the 2 nsec sample. The 2 nsec time domain data is, therefore, Fourier Transformed by adding 4 nsec (2048 points) of zeroes to the end of the original 2 nsec (1024 point) data. This process is called zero filling. In the latter case the sample transformed is a 3072 point (6 nsec) DFT. The zero filling does (1) smooth the low frequency data, (2) increase the magnitude of $\Delta\varepsilon$, and (3) make the Cole-Cole plot converge to the base line at the high and low frequency ends of the data. It does not correct ε'' enough to straighten out the negative curvature of the ε' versus (ε'' x frequency) graph.

10. Interfacial polarization between the packed solid particles may distort the data by adding another dipolar relaxation process. Bunker[1] states that this relaxation effect is too slow to affect the TDR data.

11. In a variable temperature experiment, the reference is acquired only at room temperature since the packing and unpacking of the sample cell at each temperature add in another variable, i.e. the packing effects, when one tries to compare data from different temperatures. It has been assumed by the author and by Doan[78] that the cooling of the cable would have negligible effects on the data. The time domain spectra in Figure III-14, however, demonstrate that this assumption is invalid. The top figure is a typical DIFF(t) curve for this work. The middle figure is a DIFF(t) curve for an air versus air sample at room temperature. The bottom figure is the DIFF(t) curve for the room temperature air reference data minus the waveform of air at -100 °C. The initial rise of the P(t) curve of the sample does not coincide in time with

Figure III-14. Top figure is a typical P(t) curve for the low temperature iron trimer data. The middle P(t) curve is for air versus air at room temperature, while the bottom figure is for P(t) when the air sample is acquired at -100 °C and the reference is acquired at room temperature. Notice the size of the dip in the lower P(t) curve is not negligible in reference to the top figure.


.4882
1.005
2.006
3.007
4.000
.4882
1.005
2.006
3.007
4.000
.4882
1.005
2.006
3.007
4.000

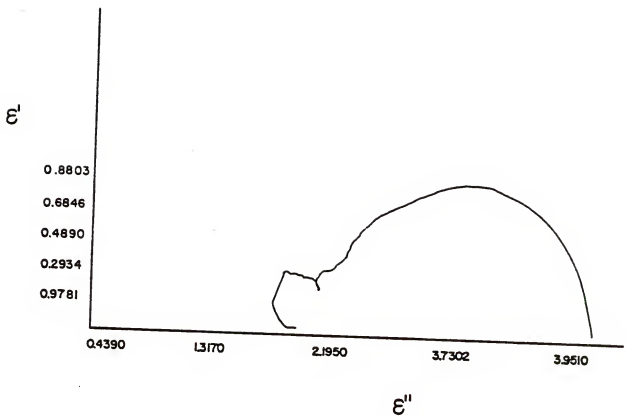
the initial dip of the P(t) curves for the air versus air curves because the latter two spectra were acquired on a different day than the P(t) data of the former. All three figures are scaled identically. One can see that the magnitude of the dip of the lower figure is not negligible in reference to the DIFF(t) curve for the solid sample in the upper most figure. At the lower temperature, this may be a source of significant error which can be minimized by using dual channel TDR (see below).

12. Even though it is insulated, the coaxial line will remove heat from the sample cell. The temperature of the sample is in thermal equilibrium with its surrounding and may, therefore, be at a higher temperature than stated. A careful temperature calibration must be carried out by placing the temperature sensing diode of the temperature control unit in the packed cell at various temperatures. The error caused by an inaccurate temperature measurement will not account for the distorted ε'' data.

13. TDR cannot accurately be used to study solid mixed valence compounds. This is surely not true. In Figure III-15 is the dispersion plot of $La_{99.995}Sr_{0.005}FeO_3$ in a 5 nsec time window. The high frequency data does have a few distortions, but the overall shape does fit an approximately semi-circular arc. (See equations I-54 - I-57 as well as Figures I-8 and I-20, for comparison to other semi-circular arcs.)

14. The sample cell responds as an RLC circuit.[56] As mentioned above, this will cause the response of the sample cell to become non-linear at some frequency determined by the sample cell and its contents. The impedance, Z, of an RLC circuit is $R - \frac{j}{\omega C} + j\omega L$,

Figure III-15. Dispersion versus absorption, or DISPA, plot for the solid extended lattice compound $La_{99.995}Sr_{0.005}FeO_3$ at room temperature in a 5 nsec window. The solid sample shows a distorted semi-circular arc which is similar in appearance to the n-propanol sample, Figure I-20. The sample was made by Doan.



$La_{99.995}\ Sr_{0.005}\ FeO_3$

5 NSEC. WINDOW

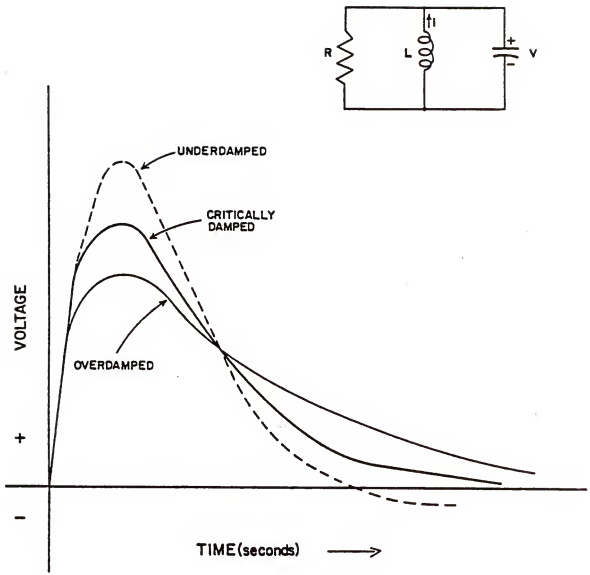
where R equals the resistance, C equals the capacitance, L equals the inductance, and j equals $\sqrt{-1}$. The impedance is the load imposed on the source voltage.

A current versus frequency graph will appear as an "S" shaped curve for an RC circuit driven by a voltage source that has constant voltage over the complete frequency range being studied. For all ratios of R/C, the curve will be smooth with no oscillations and there are no sign changes in the current or voltages; i.e., the system is "well behaved".

For TDR to work well, the "S" curve for the coaxial cable connected to the sample cell and the "S" curve for the sample cell need to be well-separated in frequency. If their frequency responses are similar, the coaxial line will attenuate the response from the sample cell. The two "S" shaped curves can be further separated by increasing the difference in their capacitance, C.

The situation becomes more complicated when inductance is added in. Then there are three possible situations: the creation of an over-damped, a critical damped, or an under-damped RLC circuit. The voltage response curve for a parallel RLC circuit is displayed in Figure III-16. The three possible situations are labeled in the figure. The underdamped circuit has a damped sinusoidal oscillation about the time axis, implying that the current and voltage change sign with time. This oscillation will cause the voltages, V(t) which equals $V_o(t)$ + R(t), to be non-linear.[58] Since the basic assumption of linearity is then no longer valid, the equations derived from it are no longer valid as well.

Figure III-16. Voltage versus time graph for the three types of parallel RLC circuit (see insert). Each curve is labeled. The under-damped curve decays to the base line faster than the other two types. Also, the under-damped circuit function contains a damped sinusoidal; thus, once the function crosses the time axis the sign of the voltage and current oscillates from negative to positive.


R
L
i
V
UNDERDAMPED
CRITICALLY DAMPED
OVERDAMPED
VOLTAGE
+
-
TIME (seconds)

When two samples are packed differently or when a solid phase change occurs within a sample, the relative magnitudes of R, L, and C may change. The RLC components of the cell and coaxial line may also change with temperature. Since Z equals $R - j/\omega C + j\omega L$, as ω is increased, the effect of the capacitive component decreases in magnitude and the effect of the inductance component increases. At some frequency the magnitude of ωL will, therefore, be greater than $1/\omega C$ and the oscillations mentioned above may become a problem. This explains why the sample becomes "poorly behaved" at high frequencies.

In summary, it is likely that the dominant problems in obtaining good data for these systems are the small $\Delta\varepsilon$ and ε_∞ of the samples and the cell acting as an RLC circuit instead of an RC circuit.

Several experiments were tried beyond the ones mentioned above to correct or minimize the effects of having samples with small $\Delta\varepsilon$ and ε_∞. These experiments are given below.

1. As mentioned above, it is difficult to characterize the dipolar relaxation process when $\Delta\varepsilon$ and ε_∞ are small since ε_∞ and $\Delta\varepsilon$ are the measured values which may be less than the actual values. The difference is the result of air being in the sample.

In an attempt to increase the measured ε_∞ or $\Delta\varepsilon$ of the sample, the inner conductor of the sample cell was made longer. The inner electrode lengths tried were: 1.5, 4.3, 5.2, and 5.5 mm in a 6.7 mm depth sample cell. The last two sample cells showed extreme sensitivity to sample depth, e.g., two sets of time domain of

methanol were acquired three minutes apart (any differences between the two sets of data should be the result of evaporation of the sample); the P(t) curves showed different exponential time constants and ε_s values. Data from these two cells which showed a sample depth dependence were not used since the effective sample depth, d, of each sample was unknown. The 4.3 mm cell was used to obtain the frequency domain water adduct spectrum shown earlier. In all cases, the measured $\Delta\varepsilon$ and ε_∞ were still small.

Increasing the length of the center electrode to increase the measured values of $\Delta\varepsilon$ and ε_∞ may lead to other problems, e.g., the longer the center electrode, the lower the high frequency cut off of f(Z) (see equation I-71). In addition, if the sample is conducting, the longer center electrode will increase the effect of conductivity on the spectrum and will increase the polarization effects of the electrodes by the sample. The increase in the effect of conductivity may also limit the high frequency cut-off. In addition, it may distort the low frequency portion of the data (derived from the time domain data as $t \to T_N$, where T_N equals the time of the time window) if the electrodes become significantly polarized by the conducting samples.

2. Another system that was attempted in order to increase the deflections of the voltage trace involved connecting a brass cap (see Efficiency Optimization section) to the sample cell. This center brass insert was connected to the brass sleeve by a screw. The insert was aligned 0.5 mm and 1.0 mm above the center electrode. The two test samples were methanol and $La_{0.995}Sr_{0.005}FeO_3$. The perovskite data had two distinct line

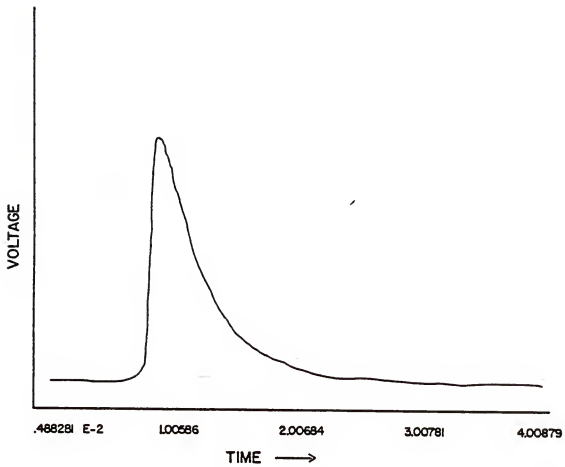
segments in the ε' versus (ε'' x frequency) graph. When the cap was added, the value of f_c for the low frequency data was decreased, while it was increased for the higher frequency data. The experiment was repeated with a sheet of teflon between the brass insert and the brass sleeve (to break electrical contact between the two parts of the cap). The calculated τ and f_c values for the sample with and without the cap were still quite different, (see Figure III-17 and III-18). With the significant variations in the exponential decay of the sample with and without the brass cap, how to interpret this data was not immediately obvious.

3. As stated above, noise was a problem since $\Delta\varepsilon$ and ε_∞ were small. In an attempt to increase the S/N ratio, three waveforms (each of which were the average of 150 scans) were averaged; however, the results were not improved for the iron trimer samples.

Suggested Experiments

Before any interpretation or comparison of the data from Mössbauer and TDR on the iron trimer system can be addressed, the question of phase transformation needs to be answered; several sets of experiments need to be carried out. First, a series of solvated and desolvated trimeric iron clusters, $[Fe_3(O)(Ac)_6X_3] \cdot y$ solvate, need to be made. Then, variable temperature FTIR and X ray crystal structure experiments on this series of complexes should be acquired. The latter two experiments should indicate: (1) how the structure of the triangle of iron centers changes with temperature, and (2) if the solvent molecules and/or the μ_3 - O

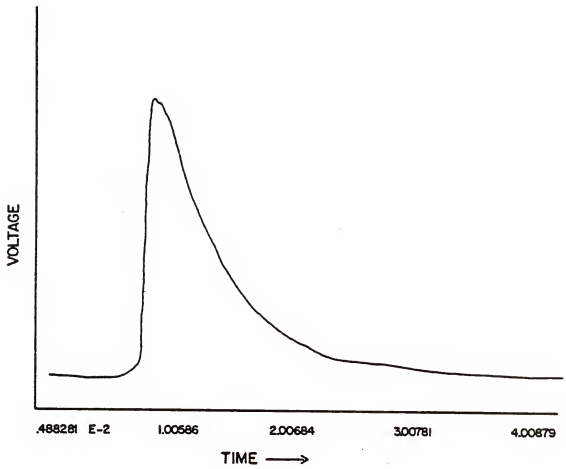
Figure III-17. The P(t) curve for $La_{99.995}Sr_{0.005}FeO_3$ at room temperature. Notice that the peak height and time to settle to the base line is greater for the sample that has the brass cap above the center electrode in Figure III-18.



$La_{99.995}\ Sr_{0.005}\ Fe\ O_3$

5 NSEC. WINDOW

Figure III-18. Same as Figure III-17 except that a brass cap has been added to the sample cell. The center brass insert of the cap is approximately 0.5 mm above the end of the center electrode.



$La_{99.995}\ Sr_{0.005}\ FeO_3$ + Cap

5 NSEC. WINDOW

group change position with temperature. This procedure will need to be done with all the variations of solvation and terminal ligands, e.g., H_2O or py. The FTIR spectrum will also need to be acquired on the non-mixed valence salt. If the μ_3 - O group is moved out of the plane of the three irons, then the orbital overlap of the irons with the bridge will be changed, as will the rate of electron transfer. In complement to the two sets of experiments given above, the heat capacity as a function of temperature needs to be determined for all the samples mentioned above. This experiment will reveal the temperatures at which there are solid phase changes. These three sets of experiments will help indicate how structural changes in the lattice affect the rate of electron transfer and what ranges of temperature can be used to derive an energy of activation for each phase of the sample.

Ruthenium Complexes

The symmetrical complex $[(bipy)_2Ru^{II}(BiBzIm)Ru^{III}(bipy)_2](PF_6)_5$ was also studied. The DIFF(t) curve shows little change from 166 - 298 K; the electron transfer rate is either too fast or too slow to be studied by TDR. Also the compound may have the non-mixed valence components mixed in since the PF_6^- salt of the (II, II) complex precipitates out of the deoxygenated water faster than the (II, III) salt did.

The asymmetric salt $[(4,4'\text{-}(MeO)_2\text{-}bipy)_2Ru^{III}(BiBzIm)Ru^{III}(bipy)_2](PF_6)_5$ needs to be tried, as its rate of electron transfer should be slower than the symmetrical complex.

CHAPTER IV
SUGGESTED IMPROVEMENTS

The present system of TDR needs to be upgraded to a dual-channel TDR. This arrangement will permit the simultaneous acquisition of the reference and sample time domain waveforms. The 7S11 sampler would be plugged into the left channel of the oscillscope (see earlier equipment section). While a power splitter splits the excitation pulse, V_o, between the two sampling heads. The pulse could then continue down the approximately matched coaxial lines to matched cells, i.e., the reference and sample cells. The two reflected pulses from the empty cells could be aligned on the 7854 oscilloscope to obtain the sum and difference of the two waveforms. The sample would then be added to one cell, and the two waveforms then added to each other by using the ADD mode of the 7854 oscilloscope, i.e., SUM(t) would be found directly from the oscilloscope. The 7S11 sampler could then be set to the inverse mode and the DIFF(t) waveform displayed on the 7854 oscilloscope.

This system of acquiring data would improve data collection in several ways. First it would decrease the noise level, allowing a weaker signal to be seen from the sample.[55] Next, it would minimize the problem of the reference being at different temperatures, since both the reference and the sample would be acquired at the same time. By the same reasoning, timing errors

should be less. An added benefit would be the removal of directional coupler from the line. This change is important because the directional coupler increases the risetime and adds extra reflections.

Another area of equipment improvement is the sample cells.[29,37,46,54,55] If one defines the magnitude of the initial time domain dip, i.e., R1 in Figure I-9, as ΔV, then for samples with small $\Delta\varepsilon$ and ε_∞, as described in this text, the objective in cell design is to produce the largest ΔV and the smallest capacitance, C, of the cell. Fulfillment of the second criteria will minimize the attenuation of the signal from the sample cell by the coaxial cable connected to the sample cell. From Chapter I, the equation relating charge and voltage of a capacitor is

$$Q = CV, \qquad \text{IV-1}$$

where Q is the charge on the electrode and V is the applied voltage. When one compares the sample and reference waveforms, he can either increase Q or decrease C in order to increse the ΔV term (see equation IV-1). In the experiment where the center electrode length was increased, the effect was to increase the total charge on the electrode. The ΔV of sample was therefore increased. As the length of the center electrode is increased, the lines of force from the central electrode to the ground electrode (outer cylinder) are spread out more. It is, therefore, likely that, for a given voltage applied to the cell, there is a critical length of the

center electrode beyond which the response of the sample will be decreased as the electrode is made longer. Also as the length of the center electrode becomes longer, the fringing field effect will become worse.

For a coaxial line, the geometric capacitance is approximately equal to[45]

$$C \doteq 2\pi\varepsilon/(\ln D/d), \qquad \text{IV-2}$$

where ε is the ε' of the material between the electrodes, D equals the diameter of the outer electrode, and d equals the diameter of the inner electrode. The capacitance of the cell can, thus, be decreased by increasing the ratio of D/d. The ΔV term may therefore be increased by increasing the diameter of the outer electrode as C decreases. Once again, there should be a critical ratio beyond which the detected response of the sample will decrease upon further increasing of the ratio. The fringing field effect is initially approximately proportional to the increase in the outer electrode diameter, e.g., if the outer electrode is doubled in size, the fringing field effect will also double.[55]

Another alternative is to increase the diameter of the center electrode. This should increase the charge on the electrode, since the surface area of the electrode is being increased. The effect of increasing the inner electrode diameter versus D/d ratio needs to be investigated.

Fringing fields are concentrated at "corners" of the

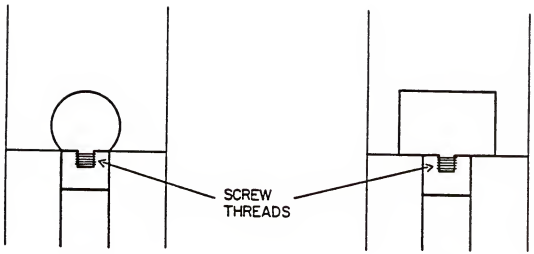
Figure IV-1. Suggested new sample cells to try.

Suggested new sample cells to try. In cells a, b, and d, the center electrode may be changed by screwing in another electrode. With all the cells, the size of the center electrode will likely have to vary, e.g., diameter variations in sample cell (a), to get the best response.

In cells a, c, and d, the sharp corners have been removed. This should decrease problems resulting from the fringing fields.

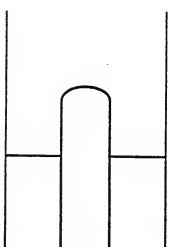
A variation of cell (a) may be tried where only a semi-sphere is used.

In cell (b), the size of the solid cylinder central conductor has been increased. This should increase the total charge on the electrode (see equation IV-1).

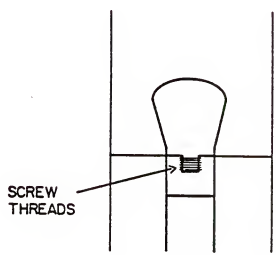


a.

b.



c.



d.

Figure IV-2. Proposed heating unit for better temperature control. A long silvered vacuum heat transfer tube is used to transfer and heat the cold N_2 gas from the copper coils to the desired temperature. The heating coil is controlled by the present temperature control unit with the temperature probe inside the sample dewar (see Figure IV-3). Both the sample dewar and the heat transfer tube need to be evacuated to at least 5×10^{-6} Torr.

HEATING UNIT

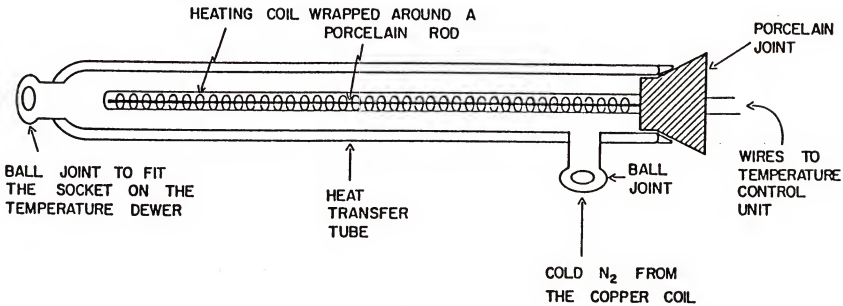
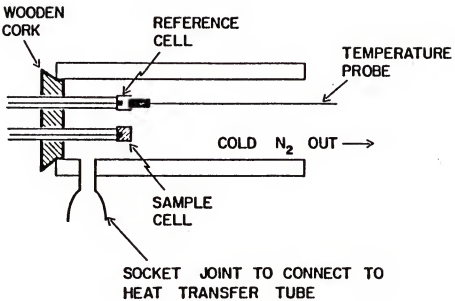
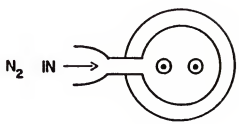

HEATING COIL WRAPPED AROUND A PORCELAIN ROD
PORCELAIN JOINT
BALL JOINT TO FIT THE SOCKET ON THE TEMPERATURE DEWER
HEAT TRANSFER TUBE
BALL JOINT
WIRES TO TEMPERATURE CONTROL UNIT
COLD N_2 FROM THE COPPER COIL

Figure IV-3. Proposed sample dewar. The size of this dewar needs to be kept to a minimum in order to reach the lower temperatures. The two cells should not be allowed to touch during the experiment.

SAMPLE DEWAR



SIDE VIEW



END VIEW

electrodes. To decrease their effect, the center electrode may be shaped as a solid semi-sphere instead of a solid cylinder. Several examples of possible cells to try are shown in Figure IV-1.[58]

If single channel TDR is used, a six dB direction coupler should replace the 10 dB one used now. The present timing marker "blip" is small; its highest point can easily be distorted by noise. There is, thus, uncertainty in its exact position. A larger timing marker would minimize this problem.

The low temperature limit of the present cooling system is too high. This problem could be solved by decreasing the size of the sample dewar and making it into a flow-through system instead of the convection cooling system presently used. (See Figure IV-2 and IV-3 for a diagram of the proposed system.)

A TDR technique where a reference of known ε' having its ε' similar in magnitude to the sample has been used with polymer solutions where $\Delta\varepsilon$ and ε_∞ are small.[54] This method is known as the difference method and may offer an alternative procedure to solve for the τ of the iron trimers.

A program suggested by Doan[79] which adds an exponential tail to the DIFF(t) data for conducting samples needs to be written. Adding an exponential tail to DIFF(t) curve to decrease truncation errors works well for non-conducting samples. It does not work for conducting samples, since $P(\infty)$ does not equal 0, i.e., $P(\infty)$ equals some finite value, A. The proper equation for this circumstance is

$$V = A + B \exp[-t/\tau], \qquad \text{IV-3}$$

where V is the voltage of the last one-third of the exponential decay portion of the DIFF(t) curve, and τ, A, and B are constants to be solved for. One may now solve for the values of V beyond the time window by substituting A, B, and τ into equation IV-3.

When noise is a problem but conductivity is not, then Gan's Windowing procedure[29] to correct for leakage error may be the correction factor of choice since it does not increase the effect of noise. The Samulon equation[29] amplifies the effect of noise, and the Nicolson ramp function[29] is awkward to work with when ω is not equal to ω_0 (see Chapter II). The problem with the Gan's Windowing procedure is that it doubles the number of time domain points in the Fourier transform.

CHAPTER V

GENERAL CONCLUSIONS AND FUTURE RECOMMENDATIONS

A good analysis of Hush theory has been presented by Bunker[1] and shall not be repeated here. Bunker proposed a modification of equation I-9 in which he replaces ε_s by ε'_{f_c}, where ε'_{f_c} is ε' at the frequency of the thermal intervalence electron transfer. This modification acknowledges that the dielectric continuum model is inadequate when the electron transfer rate is similar to solvent rotation rate. M. Weaver et al. have dealt with this problem explicitly.[87] Also Richardson has recently shown that, in at least some mixed-valence complexes, the dominant factor determining the rate of electron transfer is the solvent that the sample is in.[9] Finally, the $[Fe_3(O)(Ac)_6(4 - Etpy)_3] \cdot (Et - py)$ work mentioned earlier has shown that the presence of solvent in the lattice can profoundly affect the electron transfer rate. These statements demonstrate the importance of outersphere effects on the rates of intervalence electron transfer. When comparing data on the same compound by various techniques, especially solution phase versus solid phase, one must, therefore, be very careful not to draw rash conclusions about the electron transfer process.

As suggested by Kroeger and Bunker,[1,2,31,32] TDR should be a valid technique to measure rates of electron transfer in mixed valence solids. The equipment and equations used to analyze the time domain data have been significantly improved over those used

by Kroeger and Bunker. Even with the improvements, however, the technique does not in its present state of development work well with samples that have small numbers of charge carriers, i.e., with samples in which the measured values of $\Delta\varepsilon$ and ε_∞ are small. TDR seems to work better with mixed-valence complexes which are extended lattices where there are more charge carriers. These lattice systems and discrete metal cluster systems need to be studied further in order to better define the limitation of the equipment.

These limitations should be improved by the correct choice of sample cells. The cells are chosen such that they will yield the best compromise of the fringing field effects (the highest-high frequency cut off), the total capacitance of the cell, and the total charge of inner electrode which will produce the largest ratio of signal to noise and a large enough ΔV for the sample to be analyzable. In addition, the use of Dual Channel TDR and the Difference method of TDR should improve the response of the equipment.

The series of compounds: $[Cr_2^{III}M^{II}(O)(Ac)_6X_3]$ and $[Cr^{III}Fe^{III}M^{II}(O)(Ac)_6X_3]$, where M equals Mg, Fe, Co, and Ni and $[Fe_2^{III}M^{II}(O)(Ac)_6X_3]$, where M equals Cr, Mn, Ni, Zn[88] need to be made and tested to see the effect of the trimer being mixed metal complexes. The X ray structure of the mixed metal $[Fe_2^{III}Co^{II}(O)(Ac)_6py_3]$ shows that the metal centers were indistinguishable.[80]

It would naively appear from Dziobkowkis's work[62] that

increasing the base strength of the terminal ligand causes the rate of electron transfer to increase. It would therefore be interesting to study the series where the base strength of the terminal ligand is changed, e.g., H_2O, 4-chloro-pyridine, 4-cyano-pyridine, pyridine, ammonia, DMA, and triphenyl phosphine. The series can then be extended to $[Fe_3(B)(Y - COO)_4(Z - COO)_2X_2X']$, where B equals $O^{=}$ or $S^{=}$, Y and Z are groups with differing electron drawing ability, e.g., CF_3 and $CH_3(CH_2)_2$, and X and X' are the different terminal ligands listed above. These extensions would asymmetrize the cluster and change the electron transfer rate. The goal of studying this series would be to find some correlation between the electron withdrawing/donating ability of the ligands and the vibrations of the complexes (studied by FTIR and Raman) with the electron transfer rate.

It would also be interesting to repeat the Eu_3S_4 and $La_{1-x}Sr_xFeO_3$, where x equals 0.1, 0.2, and 0.3, work of Kroeger and Bunker and see how the frequency domain analysis differs from the time domain analysis.

APPENDIX A
COMPUTER PROGRAM TO CONVERT THE TIME DOMAIN DATA INTO FREQUENCY DOMAIN DATA

KDSAM9E.FOR..... 215

The program titled KDSAM9E.FOR calculates the frequency domain data. The time domain data are acquired from either TEKEX13.BAS or TEKSEND2.BAS. The frequency data are stored in the data file FREP015.DAT.

```
$ ASSIGN TT FOR005
$ ASSIGN TT FOR006
$ IF P1 .EQS. "" THEN INQUIRE P1 "ENTER REF. DATA FILE NAME"
$ IF P2 .EQS. "" THEN INQUIRE P2 "ENTER SAM. DATA FILE. NAME"
$ ASSIGN 'P1'.DAT FOR001
$ ASSIGN 'P2'.DAT FOR002
$ ASSIGN SUM017.DAT FOR003
$ ASSIGN DIFF016.DAT FOR004
$ ASSIGN PREP015.DAT FOR007
$ ON CONTROL_Y THEN $ GOTO DONE
$ RUN RSD$DISK:[NWJKDSAMPE.EXE
$ DONE:
$ DEASSIGN FOR001
$ DEASSIGN FOR002
$ DEASSIGN FOR003
$ DEASSIGN FOR004
$ DEASSIGN FOR007
```

```
      PROGRAM KDSAMPE
C                ORIGINAL PROGRAM BY PETE DOAN
C                REVISED BY ERNEST F. STINE JR.
C                LAST REVISION 1/7/85
C
C   LAPLACE TRANSFORMATION PROGRAM FOR SAMPLE TERMINATION TDR
C SPECTRA.
C
C   ALL CALCULATIONS THROUGH THE FOURIER TRANSFORM ARE REAL * 8
C
C   ALL THE EQUATIONS CAN BE FOUND IN : (REF 1) "FOURIER, HADAMARD,
C AND HILBERT TRANSFORMS IN CHEMISTRY" PLENUM PRESS 1982. SEE ARTICLE
C BY R. H. COLE., (REF 2) COLE, R. H., MASHIMO, S., AND WINSOR IV, P.;
C J. PHYS. CHEM. (1980) 84 p. 786, (REF 3) COLE, R. H.; J. PHYS. CHEM.
C (1980) 79 p. 1469.
C
C   THE EXPERIMENTAL DATA INPUT OF THE PROGRAM COMES FROM 2
C DIFFERENT DATA FILES:
C      FOR001    REFERENCE DATA
C      FOR002    SAMPLE DATA
C OTHER I/O IS FROM (1) INTERACTION WITH THE USER THROUGH THE
C THE TERMINAL... 4 FOR INPUT, 5 FOR OUTPUT AND (2)
C OUTPUT OF THE PROGRAM IS INTO 3 FILES:
C      FOR007    FREQUENCIES,EPSILON VALUES
C      FOR004    DIFFERENCE ARRAY
C      FOR003    SUM ARRAY
C
C   THE PROGRAM USES THE TRANSFORMS OF DIF(T) AND D(SUM(T)/DT
C IN ORDER TO SOLVE THE EQUATION
C
C   EPS=(c/d)*(R(w)-V(w))/(iw(R(w)+V(w))(F(Z))
C
C   WHERE F(Z)=ZCOT(Z).   Z=(wc/d)(EPS)**.5      -   -
C   c = SPEED OF PROPAGATION = 30 cm/nsec.
C   d = EFFECTIVE ELECTRICAL DEPTH OF SAMPLE (cm)
C   R(w) = REFLECTED WAVEFORM FROM SAMPLE
C   V(w) = REFLECTED WAVEFORM FROM REFERENCE = AIR
C   w = ANGULAR FREQENCY (RADIANS/nsec.)
C   i = SQRT(-1)
C
C WHEN THE SAMPLE IS NONCONDUCTING, F(Z) IS APPROXIMATED BY
C
C   F(Z)=1-((WC/D)**2/3)*(EPS(SAMPLE) + EPS(REFERENCE = AIR))**.5.
C
C THIS IS GOOD FOR Z ( 1 WHICH LIMITS THE VALUE OS w AND d FOR
C SAMPLES WITH LARGE EPSILON VALUES.
C
C   FOR CONDUCTING SAMPLES, THE TRANSFORM IS LIMITED TO FREQUENCIES
C WHERE F(Z)=1. THE VALUE OF EPSILON IS DETERMINED BY
C THE MODIFIED EQUATION E'=E+SIGMA/iwK.  SINCE THE VALUE OF DIF(T)
C DOES NOT APPROACH 0 AS T GOES TO INFINITY, THE TRANSFORM OF THE
C NUMERATOR IS MODIFIED TO
C
C   DIF(T)-(DIF(INF)/SUM(INF)*SUM(T)
C
C THE TRANSFORM IS DONE BY TAKING EQUALLY SPACED POINTS IN LOG(w)
C AS THE DIELECTRIC FUNCTIONS SHOULD BE SYMMETRIC IN LOG(F)
C
C      SSM    EFFECTIVE ELECTRICAL DEPTH OF SAMPLE IN cm.
C      IPS,IPR   SAMPLE AND REFERENCE TIMING MARKER ADDRESSES RESP.
C      NPS,NPR,NP    TOTAL NUMBER OF ADDRESSES USED
C      VS,VCRD    VERTICAL SCALE ON SCOPE
C      HCRD    HORIZONTAL SCALE ON SCOPE
C      TTOT    TOTAL TIME OF SAMPLE (nsec.)
C      DREF    REFERENCE DATA; THE DATA IS ORIGINALLY IN UNITS OF
C              POSITION ON THE SCOPE. CONVERT TO MILLIVOLTS.
C      DSAM    SAMPLE DATA
C      TI    TIME INTERVAL ON SCOPE
C      IP    THE SCOPE INCORRECTLY ASSIGNS THE 1st. OF THE 1st. DIVISION.
C            THIS SECTION, IP POINTS, IS REPLACED WITH A SMOOTHED AVERAGE
```

```
C          OF THE BASELINE
C      NBL  NO. OF PTS. WANTED TO DETERMINE "0" VOLTAGE OF BASELINE.  NOTE
C           THIS VALUE STARTS AT THE END OF  IP  POINTS AND NEEDS  TO END
C           BEFORE THE 1st. REFECTION PRETURBS THE WAVEFORM.
C      DIF,DSUM   DIFFERENCE AND SUMMATION DATA AFTER BASELINE CORRECTION
C      TM   TIME OF EACH PT. IN DIF AND DSUM ARRAYS.
C
       IMPLICIT REAL * 8 (A-D)
       IMPLICIT COMPLEX (Q)
       COMPLEX QSR(4096)
       REAL * 8 T,OM,OMI,OMN,RR,RS,TI,VS,R,S1,S2,TTOT,RC,HCRD,COR
       REAL * 8 THOUS,ZERO,ONE,TWO,QUART,HALF,TWENTY,DT,FREQIN
       REAL * 8 DREF(4096),DSAM(4096),DIF(4096),DSUM(4096),TM(4096)
       REAL * 8 RRE(200),RI(200),A(4096),B(4096),DDSUM(4096)
       DIMENSION  FR(4096),E1(4096),E2(4096),E3(4096),
     *QEPS(4096)
       REAL CD,DC
       INTEGER FLAG,Z,PW,M
       WRITE (5,*) '              PROGRAM KDSAM9E.FOR'
       WRITE (5,*) '              PROGRAM KDSAM9E.FOR'
       WRITE (5,*) '              PROGRAM KDSAM9E.FOR'
       THOUS  = DBLE(1000.0)
       ZERO   = DBLE(0.0)
       ONE    = DBLE(1.0)
       TWO    = DBLE(2.0)
       QUART  = DBLE(.25)
       HALF   = DBLE(.5)
       TEN    = DBLE(10.0)
       TWENTY = DBLE(20.)
       RZERO  = 0.
       RONE   = 1.
       RTWO   = 2.
       RTHIRT = 30.
       IONE   = 1
       PI     = 3.141592654
       WRITE (5,*)' ENTER NO. OF PT. TO SKIP FROM BEGINNING OF
     *TIMEWINDOW '
       READ(6,*) IP
C                          INPUT AND SCALE DATA
C**************************************************************************
C**************************************************************************
       WRITE (5,*) '                 REFERENCE INPUT MATERIAL'
       WRITE (5,*) ' EFFECTIVE DEPTH IN cm.  '
       READ(6,*) SSM
           READ(1,*) NPR
           READ (1,*) VS
           READ (1,*) HCRD
           TTOT = TEN * HCRD
       WRITE (5,*) ' VERTICAL SCALE ON SCOPE  (mV) '
       WRITE (5,*) VS
       WRITE (5,*) ' TTOT (nsec.)   P/W '
       WRITE (5,*) TTOT,NPR
C      CONVERT TO MILLIVOLTS
       VS = VS / THOUS
           DO 10 K = 1 ,NPR
                READ(1,*) DREF(K)
                DREF(K) = VS * DREF(K)
 10        CONTINUE
       WRITE (5,*) '  REFERENCE DATA DONE'
       WRITE (5,*) '        '
       WRITE (5,*) '        '
       WRITE (5,*) '                 SAMPLE INPUT MATERIAL'
           READ(2,*) NPS
           READ(2,*) VCRD
           READ(2,*) HCRD
           DO 30 K = 1 , NPS
                READ(2,*)  DSAM(K)
                DSAM(K)= VS *  DSAM(K)
 30        CONTINUE
       WRITE (5,*) ' SAMPLE DATA DONE'
C**************************************************************************
C**************************************************************************
       WRITE (5,*) '        '
       WRITE (5,*) '        '
       TI = TTOT/(DBLE(NPR)- ONE)
```

```
      NP=NPS
      WRITE (5,*) ' NO. OF PTS. WANTED TO DETERMINE "0"
     *VOLTAGE OF BASELINE '
       READ (6,*) NBL
       WRITE (5,*) '     '
       WRITE (5,*) '     '
C
C                SHIFTING SPECTRA TO MATCH TIMEING MARKERS
C**********************************************************************
C**********************************************************************
      WRITE (5,*) 'INPUT TIMEING MARKER IN nsec. (1) OR ADDRESSES (2),'
      WRITE (5,*) 'OR NO TIMEING MARKER (0)'
      READ (6,*) IT
      IF (IT .NE. 0) THEN
      IF (IT .EQ. 2) THEN
           WRITE (5,*) 'INPUT TIMING MARKER ADDRESSES: REF, SAMPLE'
           READ (6,*) IPR
           READ (6,*) IPS
      ELSE
           WRITE (5,*) 'INPUT TIMING MARKER TIME (nsec): REF, SAMPLE'
           READ (6,*) RIPR
           READ (6,*) RIPS
           SCALE = REAL(NPS) / REAL(TTOT)
           IPR = NINT(RIPR * SCALE)
           IPS = NINT(RIPS * SCALE)
           WRITE (5,*) 'REFERENCE POSITION ',IPR
           WRITE (5,*) 'SAMPLE POSITION ',IPS
      END IF
           ID = ABS(IPS - IPR)
C     ID = NO. OF PTS TO SHIFT
      IF (IPR .GT. IPS) THEN
C          REF IS SHIFTED TO RIGHT OF SAMPLE
C          REMOVE PTS. FROM BEGINNING OF REF, AND ADD PTS. TO ITS END
           CALL SHIFT(ID,DREF,NPR)
      ELSE
C          SAMPLE IS SHIFTED TO RIGHT OF REFERENCE
C          REMOVE PTS. FROM BEGINNING OF SAMPLE, AND ADD PTS. TO ITS END
           CALL SHIFT(ID,DSAM,NPR)
      END IF
      ELSE
      END IF
C
C                    BASELINE AND BASELINE CORRECTIONS
C**********************************************************************
C**********************************************************************
C
C     THE BASELINE OF SAM AND REF ARE SET TO THE SAME VALUE (0)
C     BEFORE THE SUM AND DIF ARRAYS ARE MADE. THE ORIGINAL
C     BASELINE POSITION ARE BOTH NEGATIVE VALUES.
C     BSS = BASELINE SAM
C     BSR = BASELINE REF
C
      BSS = ZERO
      BSR = ZERO
      NOP = IP + NBL
C     SMOOTH BASELINE 40,4 TIMES TO REMOVE DISTORTIONS DUE TO THE
C     TIMING MARKER AND THE RANDOM VALUE OF THE INITIAL POINTS.
C     THESE DISTORTIONS WILL CAUSE FALSE HIGH FREQ. DATA.
C
      JST = IP + 1
      ILOOP = 40
C
C     SMOOTH  NBL  PTS. OF SAMPLE AND REF,  ILOOP  TIMES STARTING
C     AT THE  JST  PT.
      CALL SMOOTH(NBL,DSAM,DREF,ILOOP,JST)
      DO 57 INDEX = 1,2
C     FIND AVERAGE BASELINE VALUE AFTER THE IPth. POINT
C
         DO 50 K = 1 , NBL
              IX = K + IP
              BSS=BSS + DSAM(IX)
              BSR=BSR + DREF(IX)
 50      CONTINUE
         BSS = BSS / (DBLE(NBL))
         BSR = BSR / (DBLE(NBL))
```

```
C         SET THE 1st. IP POINTS TO THE AVERAGE VALUE - BSS OR BSR
          DO  55 K = 1,IP
                   DSAM(K) = BSS
                   DREF(K) = BSR
 55       CONTINUE
C         SMOOTH BASELINE 6 TIMES TO REMOVE DISTORTIONS
C
          ILOOP = 6
          IF (INDEX .EQ. 1) THEN
               BSS = ZERO
               BSR = ZERO
               CALL SMOOTH(NOP,DSAM,DREF,ILOOP,IONE)
         ELSE
         END IF
 57   CONTINUE
C*****************************************************************
C*****************************************************************
       BBC1 = BSS-BSR
       BBC2 = BSS+BSR
         DO 60 K = 1 , NP
              DIF(K)  = DREF(K) - DSAM(K) + BBC1
              DSUM(K) = DREF(K) + DSAM(K) - BBC2
              TM(K+1)=DBLE(K) * TI
 60       CONTINUE
          DIF(1)   = ZERO
          DSUM(1)  = ZERO
          TM(1)    = ZERO
C
C      FOR THE DSUM AND DIF ARRAYS IT IS BEST NOT TO SMOOTH MORE THAN
C      TWICE AS THE DATA WILL BECOME SMEARD OUT WITH LOSS OF HIGH
C      FREQ. RESOLUTION.
       WRITE (5,*) '      NO. OF SMOOTHING ITERATIONS (0,1,2 OR 3)    '
       WRITE (5,*) ' FOR THE SUM AND DIFF CURVES'
       READ(6,*) I
       IF (I .NE. 0) THEN
            CALL SMOOTH(NPR,DIF,DSUM,I,IONE)
       ELSE
       END IF
C
       COR = ZERO
       FLAG = 0
       RR = ZERO
       RS = ZERO
       TY = REAL(TI) * REAL(NP -1)
C
C      AVERAGE LAST 20 PTS. OF DIF AND DSUM ARRAYS TO GET CORRECTION
C      FACTOR FOR CONDUCTIVITY. P(INF) / Q(INF)
C
       DO 110 J = 0 , 19
            II= NP-J
           RS=RS+DIF(II)
           RR=RR+DSUM(II)
 110   CONTINUE
           RR = RR / TWENTY
           RS = RS / TWENTY
       WRITE (5,*)' FINAL VALUES FOR DSUM AND DIF ARRAYS (RR,RS)'
       WRITE (5,*) RR,RS
       WRITE (5,*) '    '
       WRITE (5,*) ' INITIAL VALUES FOR DSUM AND DIF ARRAYS BEFORE
     * BASELINE CORRECTION.'
       WRITE (5,*) BSR,BSS
       WRITE (5,*) '    '
          COR = RS/RR
       WRITE (5,*) ' COND. CORRECTION FACTOR   ',COR
       WRITE (5,*) 'DO YOU WISH THIS SAMPLE TO BE CONSIDERED
     *CONDUCTING (1=Y)'
          READ(6,*) IT
          IF (IT .EQ. 1) THEN
          FLAG = 1
       WRITE (5,*) 'COND. CORRECTION FACTOR. INPUT "0" FOR THE
     *DISPLAYED VALUE. '
       READ(6,*) RC
          IF (RC .NE. 0)   COR = RC
          SG = 2.652E-3 * REAL(COR/SSM)
          DO 120 J = 1 , NP
```

```
            DIF(J) = DIF(J) - COR * DSUM(J)
 120        CONTINUE
        ELSE
        END IF
C
        WRITE (5,*)'  WISH TO ADD AN EXPONENTIAL TAIL ? (1 = Y)'
        READ (6,*) ITAIL
        IF (ITAIL .EQ. 1) THEN
        WRITE (5,*) ' DIFF = A * EXP(-t / TAU)'
        WRITE (5,*) ' INPUT A'
        READ (6,*) DPREXP
        WRITE (5,*) ' INPUT TAU'
        READ (6,*) DTAU
        WRITE (5,*) ' INPUT NO. OF nsec. TO ADD'
        READ (6,*) RNSEC
        NPDIF1 = REAL(NP) * RNSEC / REAL(TTOT) + NP
        NPR1 = NPR + 1
        DAVG = ZERO
        DO 137 K = 0,19
 137        DAVG = DREF(NPR - K) + DAVG
        DAVG = DAVG / TWENTY
        DTAVG = TWO * DAVG
        DTITAU = -TI / DTAU
        DO 138 K = NPR1,NPDIF1
           DIF(K) = DPREXP * EXP(DTITAU * DBLE(K))
 138       DSUM(K) = DTAVG - DIF(K)
        NP = NPDIF1
        ELSE
        END IF
        NPINIT = NP
        WRITE (5,*) 'WISH TO DOUBLE WINDOW SIZE BY ADDING
     * RR AND RS TO '
        WRITE (5,*) ' END OF DIFF AND SUM ARRAYS. '
        WRITE (5,*) ' THIS CAN NOT BE USED WITH COND. SAMPLES'
        WRITE (5,*) ' OR SYSTEMS WHERE TOTAL NO. OF PTS.
     * EXCEEDS 4096'
        WRITE (5,*) ' (1 = YES) PRESENT NO. OF PTS = ',NP
        READ (6,*) IZFILL
        IF (IZFILL .EQ. 1) THEN
        NWIND2 = 2 * NP
        NWIND1 = NP + 1
        WRITE (5,*) 'WISH TO ASSIGN DIF(T) AND SUM(T) = ZERO
     * (1 = Y) ?'
        READ (6,*) IZERO
        WRITE (5,*) 'WISH TO ADD ANOTHER 1 K PTS ? (1 = Y)'
        READ (6,*) IK
        IF (IK .EQ. 1) NWIND2 = NWIND2 + 1024
        DO 139 K = NWIND1,NWIND2
           IF (IZERO .EQ. 1) THEN
           DIF(K) = ZERO
           DSUM(K) = ZERO
           TM(K+1) = DBLE(K) * TI
            ELSE
           DIF(K) = RS
           DSUM(K) = RR
           TM(K+1) = DBLE(K) * TI
           END IF
 139       CONTINUE
         NP = NWIND2
          WRITE (5,*) 'NO. OF PTS. IN TIME DOMAIN    ',NP
        ELSE
        END IF
C
        WRITE (5,*) '    '
        WRITE (5,*) 'WISH DIFF AND DSUM ARRAY SENT TO DISK, 1 = YES  '
        READ(6,*) IDISU
        IF (IDISU .EQ. 1) CALL SEND(NPR,VCRD,HCRD,DIF,TM,DSUM)
        WRITE (5,*) '    '
        WRITE (5,*) '    '
        WRITE (5,*)'      DO YOU WISH A PRINT OUT OF Hs TO
     * radians, 1 = Y'
        READ(6,*) M
        IF (M .EQ. 1) CALL PFREQ
C*****************************************************************
C*****************************************************************
```

```
C
C     NFR    NO. OF FREQ. PTS. IN TRANSFORM
C     OMN    MIN. FREQ (RADIANS/nsec.)
C     OMI    MAX. FREQ.
C     DOM    EXPONENTIAL FREQ. INCREMENT
C     DT     TIME SHIFT IN nsec. FURTHER THAN 2d/c.  THE 2d/c CORRECTION
C            IS TAKEN CARE OF IN THE TRANSFORM.
C
C     THE DIFFERENCE DATA USES THE DISCRETE FOURIER TRANSFORM
C
C                          N
C     DIF(w) = TI * SUM [DIF(n * TI) * EXP(-j * w * n * TI)]
C                   n = 1
C
C     WHERE EXP(iwt) = cos(wt) - i * sin(wt) = EI
C
C     The SUM is solved by the Samulon eq. to correct for leakage.
C
C                                                  N
C                  PHI * EXP(i * phi) * SUM [(DSUM(J)-DSUM(J-1)) * EI]
C                                       J = 1
C     iwDSUM(w) = ------------------------------------------------------
C                                        SIN(PHI)
C
C     THE CORRECTION FOR 2d/c IS:
C
C                                (1 - X**2 * EPS(REF)) * EPS(APP)
C     EPS - EPS(REF) = ------------------------------------------------
C                      I - X**2 * EPS(REF) * (EPS(APP) + .33333333)
C
C     WHERE EPS(REF) = ESP OF AIR
C                c     DIF(w)
C     EPS(APP) = --- * -------
C               iwd    DSUM(w)
C     X = wd/c
C
C     THE EXTRA TIME CORRECTION IS MADE BY:
C
C     EPS = E(APP) + c/wd * tan(w * dt/ 2.) * F(Z)
C           ---------------------------------------
C           I - wd/c * tan(w * dt/ 2.) * E(APP)
C
C     WHERE E(APP) = c  *  (v - r')
C                          ---------------
C                          iwd * (v + r')
C     r' meas. sample reflected pulse.
C     dt   the time delay beyond 2d/c
C
      ZZ = 0.3333333
      QZZ = CMPLX(ZZ,RZERO)
      WRITE (5,*) '     '
      WRITE (5,*) ' NO. OF FREQUENCY POINT, MIN. AND MAX. VALUES IN
     *RADIANS PER nsec.'
      WRITE (5,*) '                DEFAULT VALUES,NO. PT =50, MIN=5MHz,
     *MAI=5GHZ'
      WRITE (5,*) '                INPUT "0" FOR DEFAULT VALUES'
      WRITE (5,*) '                ENTER (CR) AFTER EACH PT'
      READ(6,*) NFR
      READ(6,*) OMN
      READ(6,*) OMI
          IF (NFR .EQ. 0)  NFR = 50.
          IF (OMN .EQ. 0)  OMN = 3.141592654D-2
C     IF (OMI .EQ. 0)  OMI = 7.854D1
          IF (OMI .EQ. 0)  OMI = 3.141592654D1
      WRITE (5,*) ' NFR,OMN,  ', NFR,OMN
      WRITE (5,*) ' OMI  ', OMI
          DOM = EXP(LOG(OMI/OMN)/(DBLE(NFR)- ONE))
      WRITE (5,*) ' DOM    ', DOM
                OM=OMN
              NFRD3 = NFR
      WRITE (5,*) ' WISH TO DOUBLE DENSITY FTS. IN HIGH FREQ ?
     * (1 = Y)'
      READ (6,*) IPREC
      IF (IPREC .EQ. 1) THEN
```

```
C      DOM YIELDS A LOG FREQ. AND FREQIN YIELDS A LINEAR FREQ.
C      DISTRIBUTION.
       DFFREQ = OMX - OMN
       DOMN2 = OMN + DFFREQ / TWO
       NFRD2 = NFR/2
       FREQIN = (OMX - DOMN2) / DBLE(NFRD2 -1)
       INIT = NFR + 1
       IFINAL = NFR + NFRD2 + 1
       DO 145 K = INIT, IFINAL
           FR(K) = REAL(DOMN2)
 145       DOMN2 = DOMN2 + FREQIN
       NFR = NFR + NFRD2
       ELSE
       END IF
       WRITE (5,*) ' WISH A DELAY GREATER THAN 2d/c (nsec.)? ENTER (0)
      * FOR NO CHANGE.'
       READ (4,*) DT
       WRITE (5,*) '  TRANSFORMATION IN PROGRESS'
C
C
C         CD      c/d (cm/nsec./cm)
C         DC      (d/c)**2
C         DC1      2d/c
C         QCDW    c/dw
C         QSR     (dw/c)**2
C         QSR1    (dw/c)**4
C         PHI     w * TI / 2.
C         QEXP    EXP(PHI)
C         QPHISI  PHI/SIN(PHI)
C         QEP     APPARENT EPSILON BEFORE TIME SHIFT CORRECTION
C         QEPS    EPSION
C
          CD =    RTHIRT / SSM
          DC =    RONE / CD
          DC =    DC * DC
          QONE = CMPLX(RONE,RZERO)
          QREF = QONE
          NPD1 = NP - 1
          NFRD3 = NFRD3 + 1
          DO 146 J = 1,NPD1
 146         DDSUM(J) = DSUM(J+1) - DSUM(J)
          DDSUM(NPINIT) = DDSUM(NPINIT - 1)
          DO 150 K = 1 , NFR
             IF (K .GT. NFRD3) OM = DBLE(FR(K))
             A1    = ZERO
             A2    = ZERO
             B1    = ZERO
             B2    = ZERO
             ROM   = REAL (OM)
             QCDW = CMPLX(CD/ROM,RZERO)
             QDCW = CMPLX(ROM/CD,RZERO)
             IF(K .LT. NFRD5) FR(K) = ROM
             QSR(K) = CMPLX(DC * ROM * ROM,RZERO)
             QSQR= QSR(K)
             QSR1 = QSQR * QSQR
             PHI  = REAL(OM * TI / TWO)
             QPHI = CMPLX(RZERO,PHI)
             QEXP = EXP(QPHI)
             QPHISI=CMPLX(PHI/SIN(PHI),RZERO)
             DO 160 J = 1 , NPD1
                    T  = TM(J) * OM
                    D  = DIF(J)
                    D1 = DDSUM(J)
                    D2 = COS(T)
                    D3 = SIN(T)
                    A1 = A1 + D  * D2
                    B1 = B1 - D  * D3
                    A2 = A2 + D1 * D2
                    B2 = B2 - D1 * D3
 160         CONTINUE
             A1  = REAL(TI * A1)
             B1  = REAL(TI * B1)
             QA  = CMPLX(A1,B1)
             QFW = QPHISI * QEXP * CMPLX(A2,B2) / CMPLX(RZERO,ROM)
```

```
                QEP = QCDW * QA /(CMPLX(RZERO,RONE) * QFW)
                QEPS(K) = (QONE - QSQR * QREF) * QEP /
     *(QONE - QSQR * QREF * (QEP + QZZ))
                IF (DT .NE. 0.) THEN
                    D  = DT * QM / TWO
                    D1 = TAN(D)
                    QD  = CMPLX(REAL(D1),RZERO)
                    QEPS(K) = (QEPS(K) + QCDW * QD) /  (QONE - QDCW *
     *QD * QEPS(K))
                ELSE
                END IF
                QM=QM+DQM
  150       CONTINUE
            IF (FLAG .EQ. 1) THEN
        WRITE (5,*)' CONDUCTIVITY CORRECTION IN PROGRESS '
            ONE = 1.
            DO 170 K = 1 , NFR
                A(K) = REAL(QEPS(K))
                B(K) = AIMAG(QEPS(K))
                E1(K)= ( ONE  + COR) * (A(K) +  ONE )
                E2(K)= ( ONE  + COR) * B(K)
  170       CONTINUE
        WRITE (5 ,*) ' SAMPLE HAS NONZERO CONDUCTANCE OF     ',SG
        ELSE
C
C   EPS - ER = Q (1 - A(EPS+EF) - B(EPS+ER)**2)
C     where: ER = EPS FOR REFERENCE
C            Q = EPS WITH f(z) = 1.
C            A = (1/3)*(wd/c)**2
C            B = (1/45)*(wd/c)**4
C            E1 = Q - ER
C            E2 = A*(ER - E1)**2 + E1
C            E3 = E2 - E2 * B * (E2 + ER)**2 + ER
C
        WRITE (5,*)' f(Z) CORRECTION IN PROGRESS '
            QFF = CMPLX(1.0/45.,0.)
            QONE = CMPLX(1.,0.)
            DO 180 K = 1 , NFR
                QEP = QEPS(K)
C                                EPS#1
                QA = QZZ * QSR(K)
                QB = QFF * QSR(K) * QSR(K)
                QEP2=QEP*(QONE+QA*QREF) +QREF
                QEP2 = QEP2/(QONE + QA*QEP)
                QEPS(K)=QEP2*(QONE-QB*(QEP2+QREF))
                E1(K)  = REAL(QEPS(K))
                E2(K) = AIMAG(QEPS(K))
  180       CONTINUE
        WRITE (5,*) ' SAMPLE SHOWS NO CONDUCTANCE'
        END IF
            C = 2 * PI
            DO 190 K = 1 , NFR
            E3(K) = REAL(FR(K))/C
            WRITE(7,*) FR(K),',',E1(K),',',E2(K),',',E3(K)
  190       CONTINUE
        WRITE (5,*) ' TIME PER ADDRESS IN nsec. (TI)   ',TI
        WRITE (5,*) '   TIME AFTER TIMING MARKER  (TY)  ',TY
        WRITE (5,*) '    TIME INCREMENT FOR FREQ. INDEX  (DQM)  ',DQM
        WRITE (5,*) '   '
        WRITE (5,*) '   '
        WRITE (5,*) '  OMEGA MIN          OMEGA MAX         NO. OF FREQ. PT'
        WRITE (5,*) QMN,QMX,NFR
        END
C                          SMOOTHING ROUTINE
C*****************************************************************************
C*****************************************************************************
C
C
C     THE DATA IS SMOOTH BY THE ALGORITHM BELOW FOR 1 OR 2 SMOOTHINGS.
C
C     A(K) = [A(K-1) + 2*A(K) + A(K+1)]/4.
C
C     A(K) = [A(K-2)+ 4*A(K-1) + 6*A(K) + 4*A(K+1) + A(K+2)]/16.
C
      SUBROUTINE SMOOTH(NPR,DIF,DSUM,ILOOP,L)
      IMPLICIT DOUBLE PRECISION (A-D)
```

```
      REAL *8 TWO,QUART,R,HALF
      DIMENSION DIF(4096),DSUM(4096)
C COMMON /BLK2/ TWO,QUART,HALF
      TWO   = DBLE(2.0)
      QUART = DBLE(.25)
      HALF  = DBLE(0.5)
      IST = NPR - 2
      L01 = L + 1
      L02 = L + 2
      NP1 = NPR - 1
      DO 90 K = 1 , ILOOP
            A1=DIF(L)
            A2=DIF(L01)
            DQ=A1+ TWO *A2+DIF(L02)
            B1=DSUM(L)
            B2=DSUM(L01)
            R=B1+ TWO *B2+DSUM(L02)
            DO 100 J = L01 , IST
                J1 = J + 1
                J2 = J + 2
                DIF(J)  = QUART * DQ
                DSUM(J) = QUART * R
                DQ=DQ+DIF(J1)+DIF(J2)-A1-A2
                R=R+DSUM(J1)+DSUM(J2)-B1-B2
                A1=A2
                A2=DIF(J1)
                B1=B2
                B2=DSUM(J1)
100         CONTINUE
            DIF(NP1) = QUART * DQ
            DSUM(NP1)= QUART * R
            DIF(NPR) = HALF * (A2 + DIF(NPR))
            DSUM(NPR)= HALF * (B2 + DSUM(NPR))
            DIF(L)   = HALF * (DIF(L)  + DIF(L01))
            DSUM(L) = HALF * (DSUM(L) + DSUM(L01))
90       CONTINUE
      RETURN
      END
C                        SHIFTING ROUTINE
C*********************************************************************
C*********************************************************************
      SUBROUTINE SHIFT(ID,DSAM,NPR)
      REAL *8 RR,DSAM
      DIMENSION DSAM(4096)
      IDNP = NPR - ID
      ID1 = ID - 1
      RR = DBLE(0.)
      DO 2000 K = 0,3
2000        RR = RR + DSAM(NPR - K)
      RR = RR /  DBLE(4.)
      DO 2010 K = 1,IDNP
2010        DSAM(K) = DSAM(ID + K)
      DO 2020 K = 1,ID
2020        DSAM(K + IDNP) = RR
      RETURN
      END
C                        CALCULATE FREQ. IN Hz.
C*********************************************************************
C*********************************************************************
      SUBROUTINE FFREQ
      DIMENSION OHZ(2),OR(2)
      PI = 3.141592654
      OHZ(2) = 0.
      OR(2)  = 0.
      WRITE (5,*) 'NO OF FREQ. TO CONVERT, 1 OR 2  '
      READ(6,*) IJ
      OA = 2 * PI
      DO 210 I = 1 , IJ
      WRITE (5,*) 'FREQ. IN Hz    '
      READ(6,*) OHZ(I)
      OR(I) = OHZ(I) * OA/1E9
210   CONTINUE
      WRITE (5,*) '    HZ(1)     R/nsec   HZ(2)    R/nsec '
      WRITE (5,*) OHZ(1),OR(1),OHZ(2),OR(2)
      RETURN
```

```
      END
C                  SENDING SUM AND DIFF TO DISK
C*********************************************************************
C*********************************************************************
      SUBROUTINE SEND(NPR,VCRD,HCRD,DIF,TM,DSUM)
      REAL * 8 DIF(4096),DSUM(4096),TM(4096),HCRD
      WRITE (5,*) '  SENDING DSUM AND DIFF ARRAY TO DISK'
          WRITE (4,*) NPR
          WRITE (4,*) VCRD
          WRITE (4,*) HCRD
          DO 130 J = 1 , NPR
              WRITE(4,*) DIF(J),',',TM(J)
130       CONTINUE
          WRITE (3,*) NPR
          WRITE (3,*) VCRD
          WRITE (3,*) HCRD
          DO 145 J = 1, NPR
              WRITE(3,*) DSUM(J),',',TM(J)
145       CONTINUE
      RETURN
      END
```

APPENDIX B
COMPUTER PROGRAMS USED FOR THE BILINEAR CORRECTION FACTOR

COLE26.FOR..... 227

ICOLE26.FOR..... 231

The program titled COLE26.FOR calculates the complex parameters, A, B, and C, for the bilinear correction factor. The program titled ICOLE26.FOR calculates the corrected frequency domain data by using the parameters from the program titled COLE26.FOR.

```
$ ASSIGN COLE8.DAT FOR004
$ ASSIGN TT FOR005
$ ASSIGN TT FOR006
$ ASSIGN COLE5.DAT FOR010
$ ASSIGN COLE6.DAT FOR011
$ ASSIGN COLE7.DAT FOR009
$ IF P1 .EQS. "" THEN INQUIRE P1 "ENTER STAND. 1 DATA FILE NAME"
$ IF P2 .EQS. "" THEN INQUIRE P2 "ENTER STAND. 2 DATA FILE NAME"
$ IF P3 .EQS. "" THEN INQUIRE P3 "ENTER STAND. 3 DATA FILE NAME"
$ ASSIGN 'P1'.DAT FOR001
$ ASSIGN 'P2'.DAT FOR002
$ ASSIGN 'P3'.DAT FOR003
$ ON CONTROL_Y THEN $ GOTO DONE
$ RUN RSD$DISK:[ES]COLE26.EXE
$ DONE:
$ DEASSIGN FOR001
$ DEASSIGN FOR002
$ DEASSIGN FOR003
$ DEASSIGN FOR004
$ DEASSIGN FOR010
$ DEASSIGN FOR011
$ DEASSIGN FOR009
```

```
C
      PROGRAM COLE26
C                          DOUBLE PRECISION VERSION
C
C
C          SOLVES COLE'S EQ. TO CORRECT FOR MISMACHES IN THE INSTRUMENT
C        FROM "IEEE TRANSACTIONS ON INSTRUMENTATION AND MEASUREMENT",
C        VOL IM-32,NO. 1, MARCH 1983      p. 42
C
C          TRUE EPS(K) = A * (MEAS. EPS(K)) + C
C                        ------------------------                    eq. 1.
C                        1 - B * (MEAS. EPS(K))
C
C            WHERE A,B,C ARE COMPLEX NO.
C
C          TRUE EPS(K) COMES FROM EQ. IN: "DIELECTRIC PROPERTIES AND
C        MOLECULAR BEHAVIOR" BY N E. HILL, W.E. VAUGHAM, A.H. PRICE, AND
C        M. DAVIES"  VAN NOSTRAND REINHOLD COMPANY, LONDON (1969) p. 48
C
C            REAL =      E0 -  EINF                  EINF
C                        ----------------     +                     eq. 2
C                        1 + (w * Tau)**2
C
C            IMAGINARY = (w * Tau) * (E0 - EINF)
C                        --------------------------                  eq. 3
C                            1 + (w * Tau)**2
C
C        FR()    = ANGULAR FREQ. IN RADIANS PER nsec.
C        E1(i,j) = E1 OF REFERENCE  "i"  AT FREQ. "FR(j)"
C          E1(i,K) = MEASURED REAL  PART OF REFERENCE # 1 AT FREQUENCY FR(K)
C          E2(i,K) = ----"--  IMAG.  ----"----"----"----"----"----"----
C        RT1  = CALCULATED REAL  PART OF REFERENCE  "i" AT FREQ. "FR(j)"
C        IREPS(i,j) = CALCULATED IMAG. PART OF REFERENCE  "i" AT FREQ. "FR(j)"
C        NFR = # OF FREQ. PT
C        T1     = TAU OF REFERENCE # 1
C        E01    = E0 (STATIC DIELECTRIC CONSTANT)  OF REFERENCE # 1
C        EINF1  = EINF (HIGH FREQ. DIELECTRIC CONSTANT) OF REFERENCE # 1
C        TS1    = SQUARE OF TAU - REF. # 1
C
C
C
      DOUBLE PRECISION E01,E02,E03,E1(3,200),E2(3,200),E3(200),EINF1,
     *EINF2,EINF3,F,FR(200),FRS,FRS1,FRS2,FRS3,FRT1,FRT2,FRT3,
     *LOSS1,LOSS2,LOSS3,MIL,ONE,T1,T2,T3,TS1,TS2,TS3,ZERO
        INTEGER ANSW
        REAL *8 RT1(200),RT2(200),RT3(200),IE1(200),IE2(200),IE3(200)
C
        COMPLEX A(200),B(200),C(200),R1,R2,R3,EP1,EP2,EP3,CONE,B1
C
        DATA LOSS1, LOSS2, LOSS3/0., 0., 0. /
        DATA T1, T2, T3/0., 0., 0. /
        DATA TS1, TS2, TS3/0., 0., 0. /
        DATA E01, E02, E03, ZERO/0., 0., 0., 0. /
        DATA EINF1, EINF2, EINF3/0., 0., 0./
        DATA FRS1, FRS2, FRS3/0., 0., 0./
        DATA FRT1, FRT2, FRT3,FRS/0., 0., 0., 0./
        DO 6 J = 1,200
             IE1(J) = ZERO
             IE2(J) = ZERO
             IE3(J) = ZERO
             RT1(J) = ZERO
             RT2(J) = ZERO
             RT3(J) = ZERO
6       CONTINUE
        WRITE(5,*)' NO. OF FREQ. PTS. '
        READ(6,*) NFR
        WRITE(5,*)' TAU(nsec), E0, EINF FOR STD. 1.,
     * ENTER A (CR) AFTER EACH #'
        READ(6,*) T1
        READ(6,*) E01
        READ(6,*) EINF1
        WRITE(5,*)' TAU, E0, EINF FOR STD. 2.'
```

```
      READ(6,*) T2
      READ(6,*) E02
      READ(6,*) EINF2
      WRITE(5,*)' TAU, E0, EINF FOR STD. 3.'
      READ(6,*) T3
      READ(6,*) E03
      READ(6,*) EINF3
      WRITE(5,*)'  '
C     OPEN(1,FILE= PS,ERR=30)
      DO 20 K=1,NFR
            READ (1,*) FR(K), E1(1,K), E2(1,K),E3(K)
 20   CONTINUE
C     OPEN(2,FILE=S5,ERR=50)
      DO 40 K=1,NFR
            READ (2,*) F,E1(2,K), E2(2,K)
 40   CONTINUE
C     OPEN(3,FILE=TS,ERR=70)
      DO 60 K=1,NFR
            READ (3,*) F,E1(3,K), E2(3,K)
 60   CONTINUE
C      OPEN(10,FILE='COLE5.DAT',STATUS = 'NEW')
C      OPEN(11,FILE='COLE6.DAT',STATUS = 'NEW')
C      OPEN(9,FILE = 'COLE7.DAT',STATUS ='NEW')
C
C         Tau ** 2
      TS1 = T1 * T1
      TS2 = T2 * T2
      TS3 = T3 * T3
C           E0 - EINF
      LOSS1 = E01 - EINF1
      LOSS2 = E02 - EINF2
      LOSS3 = E03 - EINF3
      ONE = 1.
      DO 90 K =1,NFR
            F = FR(K)
C                 w ** 2
            FRS = F * F
C                 (w * Tau) ** 2
            FRS1 = FRS * TS1
            FRS2 = FRS * TS2
            FRS3 = FRS * TS3
C                 (w * Tau)
            FRT1 = F * T1
            FRT2 = F * T2
            FRT3 = F * T3
            RT1(K) = LOSS1 / (ONE + FRS1) + EINF1
            IE1(K) = -(FRT1 * LOSS1) / ( ONE + FRS1)
            RT2(K) = LOSS2 / (ONE + FRS2) + EINF2
            IE2(K) = -(FRT2 * LOSS2) / ( ONE + FRS2)
            RT3(K) = LOSS3 / (ONE + FRS3) + EINF3
            IE3(K) = -(FRT3 * LOSS3) / ( ONE + FRS3)
 90   CONTINUE
C
C     OPEN(4,FILE='COLE8.DAT',STATUS = 'NEW',ERR= 78)
      RZERO = 0.
      RONE  = 1.
            DO 400 IFREQ = 1,NFR
               CONE = CMPLX(RONE,RZERO)
               EP1 = CMPLX(RZERO,RZERO)
               EP2 = CMPLX(RZERO,RZERO)
               EP3 = CMPLX(RZERO,RZERO)
               R1 = CMPLX(RZERO,RZERO)
               R2 = CMPLX(RZERO,RZERO)
               R3 = CMPLX(RZERO,RZERO)
               A(IFREQ) = CMPLX(RZERO,RZERO)
               B(IFREQ) = CMPLX(RZERO,RZERO)
               C(IFREQ) = CMPLX(RZERO,RZERO)
C                    (- cone) is due to subtracting the reference air, EPS = 1
C                    A are for meas.  R are for theo.
               EP1 = CMPLX(REAL(E1(1,IFREQ)),REAL(-E2(1,IFREQ)))
               EP2 = CMPLX(REAL(E1(2,IFREQ)),REAL(-E2(2,IFREQ)))
               EP3 = CMPLX(REAL(E1(3,IFREQ)),REAL(-E2(3,IFREQ)))
               R1 = CMPLX(REAL(RT1(IFREQ)),REAL(-IE1(IFREQ)))
               R2 = CMPLX(REAL(RT2(IFREQ)),REAL(-IE2(IFREQ)))
               R3 = CMPLX(REAL(RT3(IFREQ)),REAL(-IE3(IFREQ)))
```

```
C
                B1   = (EP1-EP3)*(R1-R2) - (EP1-EP2)*(R1-R3)
                B(IFREQ)   = B1 / ((EP1-EP3)*(R1*EP1 - R2*EP2) -
     *(EP1-EP2)*(R1*EP1 - R3*EP3))
                B1 = B(IFREQ)
                A(IFREQ)   = (B1 * (R3*EP3-R2*EP2) + R2-R3) /
     *(EP2 - EP3)
                C(IFREQ)   = R1 - (A(IFREQ) * EP1) - (B1 - EP1 * R1)
600             CONTINUE
                DO 700 K=1,NFR
                   WRITE (4,*) A(K),E3(K)
                   WRITE (4,*) B(K)
                   WRITE (4,*) C(K)
700             CONTINUE
          END
```

```
$ IF P1 .EQS. "" THEN INQUIRE P1 "ENTER A FILE NAME"
$ ASSIGN 'P1'.DAT FOR001
$ ASSIGN TT FOR005
$ ASSIGN TT FOR006
$ ASSIGN COLE8.DAT FOR004
$ ASSIGN FREP2.DAT FOR002
$ ON CONTROL_Y THEN $ GOTO DONE
$ RUN RSD$DISK:[ES]ICOLE24.EXE
$ DONE:
$ DEASSIGN FOR001
$ DEASSIGN FOR002
$ DEASSIGN FOR004
```

```
      PROGRAM ICOLE26
C       MODIFIED ICOLE7 FOR   10/26/84
C
C
C       SOLVES COLE'S EQ. TO CORRECT FOR MISMACHES IN THE INSTRUMENT
C     FROM "IEEE TRANSACTIONS ON INSTRUMENTATION AND MEASUREMENT",
C     VOL IM-32,NO. 1, MARCH 1983   p. 42
C
C       TRUE EPS(K) = A * (MEAS. EPS(K)) + C
C                     ------------------------                    eq. 1.
C                     1 - B * (MEAS. EPS(K))
C
C          WHERE A,B,C ARE THE COMPLEX CORRECTION FACTORS
C     E1() = REAL  COMPONENT OF COMPLEX DIELECTRIC CONST.
C     E2() = IMAG. ----------"-----------------------
C     NFR  = NO. OF FREQ. PT.
C     QMEPS  = MEASURED DIELECTRIC CONST.
C     QEPS() = CORRECTED DIELECTRIC CONST.
C
C
      COMPLEX A(200),B(200),C(200),QEPS(200),QMEPS,ONE,ZERO,QX
      DIMENSION FR(200),E1(200),E2(200),E3(200),F(200)
C
      ZERO = CMPLX(0.,0.)
      ONE  = CMPLX(1.,0.)
      RZERO = 0.
      DO 5 I = 1,200
            A(I) = ZERO
            B(I) = ZERO
            C(I) = ZERO
            QEPS(I) = ZERO
            FR(I) = RZERO
            E1(I) = RZERO
            E2(I) = RZERO
    5       E3(I) = RZERO
            QMEPS = ZERO
      WRITE(5,*)' ENTER NO. OF FREQ. PT'
      READ(4,*) NFR
C       OPEN (1,FILE=PS,ERR=11)
      WRITE(5,*)' ENTERING MEASURED DATA FROM DISK'
      DO 10 K=1,NFR
            READ (1,*) FR(K), E1(K), E2(K),E3(K)
   10 CONTINUE
      WRITE(5,*)' ENTERING A,B,C DATA FROM DISK'
C                 OPEN (4,FILE='COLE8.DAT',ERR=50)
      DO 40 I=1,NFR
            READ(4,*) A(I),F(I)
            READ(4,*) B(I)
   40       READ(4,*) C(I)
C                 OPEN (2,FILE='FREP2.DAT',STATUS='NEW',ERR=80)
      WRITE(5,*)' NO. CRUNCHING'
      DO 70 K= 1,NFR
            QMEPS = CMPLX(E1(K),E2(K))
            QEPS(K) = (A(K) * QMEPS + C(K)) / (ONE - B(K) * QMEPS)
C                     QEPS(K) = (((A(K) * (QMEPS-ONE)) + C(K)) /
C                       *(ONE - (B(K) * (QMEPS - ONE)))) + ONE
C             WRITE(5,*) QEPS(K)
            E1(K)= REAL(QEPS(K))
            E2(K)= AIMAG(QEPS(K))
            WRITE (2,*) FR(K),',',E1(K),',',E2(K),',',E3(K)
   70 CONTINUE
      WRITE(5,*)' DONE'
      END
```

APPENDIX C
COMPUTER PROGRAM USED FOR THE DIFF(T) DATA

DIFFER2.FOR..... 233

The program titled DIFFER2.FOR calculates the time domain difference data. The data may be manipulated as in the program titlted KDSAM9E.FOR.

```
      PROGRAM DIFFER
C
      REAL * 4 DREF(1024),DSAM(1024),DIF(3072),DSUM(1024)
      CHARACTER *15 SS,RSS
      INTEGER FLAG,Z,PW,M
      CALL CLS
      WRITE (*,*) '                PROGRAM DIFFER.FOR'
      WRITE (*,*) '                PROGRAM DIFFER.FOR'
      WRITE (*,*) '                PROGRAM DIFFER.FOR'
      THOUS  = 1000.0
      HUND   = 100.0
      ZERO   = 0.0
      TWO    = 2.0
      QUART  = .25
      HALF   = .5
      TEN    = 10.0
      TWENTY = 20.
      RZERO  = 0.
      RONE   = 1.
      RTWO   = 2.
      RTHIRT = 30.
      IONE = 1
      PI     = 3.141592654
      WRITE (*,*)' ENTER NO. OF PT. TO SKIP FROM BEGINNING OF
     *TIMEWINDOW '
      READ(*,*) IP
 1000 PRINT *, '              '
C
C      GOTO 1001
C
      PRINT *,' ENTER NAME OF REF. FILE, WITH QUOTATIONS MARKS'
      READ (*,*) RSS
C
C1001 RSS = 'REFEA6.DAT'
 2000 PRINT *, '              '
      PRINT *,' ENTER NAME OF SAMPLE FILE, WITH QUOT. MARKS'
      READ (*,*) SS
      OPEN (1,FILE = RSS,ERR = 1000)
      OPEN (2,FILE = SS,ERR = 2000)
C                          INPUT AND SCALE DATA
C*********************************************************************
C*********************************************************************
      WRITE (*,*) '                        REFERENCE INPUT MATERIAL'
         READ(1,*) NPR
         READ (1,*) VS
         READ (1,*) HCRD
         TTOT = TEN * HCRD
      PRINT *, '              '
      WRITE (*,*) ' VERTICAL SCALE ON SCOPE  (mV) '
      WRITE (*,*) VS
      WRITE (*,*) ' TTOT (nsec.)   P/W '
      WRITE (*,*) TTOT,NPR
         DO 10 K = 1 ,NPR
            READ(1,*) DREF(K)
            DREF(K) = HUND * DREF(K)
 10      CONTINUE
      PRINT *, '              '
      WRITE (*,*) '  REFERENCE DATA DONE'
      WRITE (*,*) '              '
      WRITE (*,*) ''
      WRITE (*,*) '                        SAMPLE INPUT MATERIAL'
         READ(2,*) NPS
         READ(2,*) VCRD
         READ(2,*) HCRD
         DO 30 K = 1 , NPS
            READ(2,*)  DSAM(K)
            DSAM(K)= HUND *  DSAM(K)
 30      CONTINUE
      WRITE (*,*) ' SAMPLE DATA DONE'
      CLOSE (1)
      CLOSE (2)
C*********************************************************************
C*********************************************************************
```

```
        WRITE (*,*) '       '
        WRITE (*,*) '       '
        NP=NPS
       WRITE (*,*) ' NO. OF PTS. WANTED TO DETERMINE "0"
      *VOLTAGE OF BASELINE '
       READ (*,*) NBL
       WRITE (*,*) '     '
       WRITE (*,*) '     '
C
C                  SHIFTING SPECTRA TO MATCH TIMEING MARKERS
C*****************************************************************
C*****************************************************************
       WRITE (*,*) 'INPUT TIMEING MARKER IN nsec. (1) OR ADDRESSES (2),'
       WRITE (*,*) 'OR NO TIMEING MARKER (0)'
       READ (*,*) IT
       IF (IT .NE. 0) THEN
       IF (IT .EQ. 2) THEN
            WRITE (*,*) 'INPUT TIMING MARKER ADDRESSES: REF, SAMPLE'
            READ (*,*) IPR
            READ (*,*) IPS
       ELSE
            WRITE (*,*) 'INPUT TIMING MARKER TIME (nsec): REF, SAMPLE'
C
C        GOTO 1002
            READ (*,*) RIPR
C1002 RIPR = .07617
            READ (*,*) RIPS
            SCALE = REAL(NPS) / REAL(TTOT)
            IPR = NINT(RIPR * SCALE)
            IPS = NINT(RIPS * SCALE)
            WRITE (*,*) 'REFERENCE POSITION ',IPR
            WRITE (*,*) 'SAMPLE POSITION ',IPS
       END IF
            ID = ABS(IPS - IPR)
       IF (IPR .GT. IPS) THEN
C           REF IS SHIFTED TO RIGHT OF SAMPLE
C           REMOVE PTS. FROM BEGINNING OF REF, AND ADD PTS. TO ITS END
            CALL SHIFT(ID,DREF,NPR)
       ELSE
C           SAMPLE IS SHIFTED TO RIGHT OF REFERENCE
C           REMOVE PTS. FROM BEGINNING OF SAMPLE, AND ADD PTS. TO ITS END
            CALL SHIFT(ID,DSAM,NPR)
       END IF
       ELSE
       END IF
C
C                     BASELINE AND BASELINE CORRECTIONS
C*****************************************************************
C*****************************************************************
        BSS = ZERO
        BSR = ZERO
        NOP = IP + NBL
C       SMOOTH BASELINE 80 TIMES TO REMOVE DISTORTIONS DUE TO THE
C       TIMING MARKER AND THE RANDOM VALUE OF THE INITIAL POINTS.
C       THESE DISTORTIONS WILL CAUSE FALSE HIGH FREQ. DATA.
C
       JST = IP + 1
       ILOOP = 80
       CALL SMOOTH(NBL,DSAM,DREF,ILOOP,JST)
       DO 57 INDEX = 1,2
C          FIND AVERAGE BASELINE VALUE AFTER THE IPth. POINT
C
           DO 50 K = 1 , NBL
                IX = K + IP
                BSS=BSS + DSAM(IX)
                BSR=BSR + DREF(IX)
 50        CONTINUE
           BSS = BSS / (REAL(NBL))
           BSR = BSR / (REAL(NBL))
C          SET THE 1st. IP POINTS TO THE AVERAGE VALUE - BSS OR BSR
           DO  55 K = 1,IP
                DSAM(K) = BSS
                DREF(K) = BSR
 55        CONTINUE
C          SMOOTH BASELINE TO REMOVE DISTORTIONS
```

```
C
          ILOOP = 6
          IF (INDEX .EQ. 1) THEN
              BSS = ZERO
              BSR = ZERO
              CALL SMOOTH(NOP,DSAM,DREF,ILOOP,IONE)
          ELSE
          END IF
 57    CONTINUE
C*********************************************************************
C*********************************************************************
      BBC1 = BSS-BSR
      BBC2 = BSS+BSR
          DO 60 K = 1 , NP
              DIF(K)  = DREF(K) - DSAM(K) + BBC1
              DSUM(K) = DREF(K) + DSAM(K) - BBC2
 60       CONTINUE
          DIF(1)  = ZERO
          DSUM(1) = ZERO
      WRITE (*,*) '     NO. OF SMOOTHING ITERATIONS (0,1,2 OR 3)    '
      WRITE (*,*) ' FOR THE SUM AND DIFF CURVES'
      READ(*,*) I
      IF (I .NE. 0) THEN
          CALL SMOOTH(NPR,DIF,DSUM,I,IONE)
      ELSE
      END IF
          COR = ZERO
          FLAG = 0
          RR = ZERO
          RS = ZERO
          TI = TTOT / REAL(NP - 1)
          TY = REAL(TI) * REAL(NP -1)
          DO 110 J = 0 , 19
              IX= NP-J
              RS=RS+DIF(IX)
              RR=RR+DSUM(IX)
 110      CONTINUE
          RR = RR / TWENTY
          RS = RS / TWENTY
      WRITE (*,*) ' FINAL VALUES FOR DSUM AND DIF ARRAYS '
      WRITE (*,*) RR,RS
      WRITE (*,*) '  '
      WRITE (*,*) ' INITIAL AVERAGE VALUES BASELINE REF. AND SAM.'
      WRITE (*,*) BSR,BSS
      WRITE (*,*) '  '
          COR = RS/RR
      WRITE (*,*) ' COND. CORRECTION FACTOR   ',COR
          WRITE (*,*) 'DO YOU WISH THIS SAMPLE TO BE CONSIDERED
     *CONDUCTING (1=Y)'
          READ(*,*) IT
          IF (IT .EQ. 1) THEN
          FLAG = 1
      WRITE (*,*) 'COND. CORRECTION FACTOR. INPUT "0" FOR THE
     *DISPLAYED VALUE. '
      READ(*,*) RC
          IF (RC .NE. 0)   COR = RC
          SC = 2.652E-3 * REAL(COR/SSM)
          DO 120 J = 1 , NP
              DIF(J) = DIF(J) - COR * DSUM(J)
 120      CONTINUE
      ELSE
      END IF
      BETA  = ZERO
      TAU   = ZERO
      IANSW = ZERO
      NPS = NPR
      WRITE (*,*) 'WISH DIFF ARRAY SENT TO DISK, 1 = YES  '
      READ(*,*) IDISU
      IF (IDISU .EQ. 1) CALL SEND(NPR,VCRD,HCRD,DIF,BETA,TAU)
      PRINT *,'
 130  WRITE (*,*) 'WISH EXPONENTIAL TAIL ADDED ON ? (1 = YES)'
      READ (*,*) IANSW
      IF (IANSW .EQ. 1) THEN
          CALL EXPONT(DIF,NPDIF,NP,NPS,TI,BETA,TAU)
          CALL TAIL(DIF,NPS,NP,BETA,TAU,TI)
```

```
          WRITE (*,*) ' PRE-EXPONENTIAL FACTOR  ',BETA
          WRITE (*,*) ' TAU             ',TAU
          WRITE (*,*) 'WISH TO REPEAT ADDING A TAIL (1 = YES)'
          READ (*,*) TAILNG
          IF (TAILNG .EQ. 1) GOTO 130
          WRITE (*,*) 'WISH TO SEND NEW DATA TO DISK? (1 = Y)'
          READ (*,*) SENDNG
          IF (SENDNG .EQ. 1) CALL SEND(NPS,VCRD,HCRD,DIF,BETA,TAU)
        ELSE
        END IF
        PRINT *,'  REFERENCE      ',RSS
        PRINT *,'  SAMPLE         ',SS
        PRINT *,'                 '
        PRINT *,'                 '
        PRINT *,'     DONE'
        PRINT *,'          DONE'
        PRINT *,'               DONE'
        PRINT *,'                    DONE'
        PRINT *,'               DONE'
        PRINT *,'          DONE'
        PRINT *,'     DONE'
        END
C                          SMOOTHING ROUTINE
C*****************************************************************
C*****************************************************************
        SUBROUTINE SMOOTH(NPR,RDIF,RDSUM,ILOOP,L)
        IMPLICIT REAL * 8 (A-H)
        IMPLICIT REAL * 8 (O-Z)
        REAL * 4 RDIF(1024),RDSUM(1024)
        DIMENSION DIF(1024),DSUM(1024)
        SAVE
C
        DO 70 K = 1,NPR
           DIF(K)  = DBLE(RDIF(K))
 70        DSUM(K) = DBLE(RDSUM(K))
        TWO   = DBLE(2.0)
        QUART = DBLE(.25)
        HALF  = DBLE(0.5)
        IST = NPR - 2
        L01 = L + 1
        L02 = L + 2
        NP1 = NPR - 1
            DO 90 K = 1 , ILOOP
                A1=DIF(L)
                A2=DIF(L01)
                DQ=A1+ TWO *A2+DIF(L02)
                B1=DSUM(L)
                B2=DSUM(L01)
                R=B1+ TWO *B2+DSUM(L02)
                DO 100 J = L01 , IST
                   J1 = J + 1
                   J2 = J + 2
                   DIF(J)  = QUART * DQ
                   DSUM(J) = QUART * R
                   DQ=DQ+DIF(J1)+DIF(J2)-A1-A2
                   R=R+DSUM(J1)+DSUM(J2)-B1-B2
                   A1=A2
                   A2=DIF(J1)
                   B1=B2
                   B2=DSUM(J1)
 100            CONTINUE
                DIF(NP1) = QUART * DQ
                DSUM(NP1)= QUART * R
                DIF(NPR) = HALF * (A2 + DIF(NPR))
                DSUM(NPR)= HALF * (B2 + DSUM(NPR))
                DIF(L)   = HALF * (DIF(L)  + DIF(L01))
                DSUM(L)  = HALF * (DSUM(L) + DSUM(L01))
 90         CONTINUE
            DO 110 K = 1,NPR
                RDIF(K)  = REAL(DIF(K))
 110            RDSUM(K) = REAL(DSUM(K))
            RETURN
            END
C                          SHIFTING ROUTINE
C*****************************************************************
```

```
C*****************************************************************
      SUBROUTINE SHIFT(ID,DSAM,NPR)
      REAL *4 RR,DSAM
      DIMENSION DSAM(1024)
      SAVE
      IDNP = NPR - ID
      ID1 = ID - 1
      RR = 0.
      DO 2000 K = 0,3
 2000       RR = RR + DSAM(NPR - K)
      RR = RR / 4.
      DO 2010 K = 1,IDNP
 2010       DSAM(K) = DSAM(ID + K)
      DO 2020 K = 1,ID
 2020       DSAM(K + IDNP) = RR
      RETURN
      END
C                     CALCULATE FREQ. IN Hz
C*****************************************************************
C*****************************************************************
      SUBROUTINE PFREQ
      DIMENSION OHZ(2),OR(2)
      PI = 3.141592654
      OHZ(2) = 0.
      OR(2)  = 0.
  200 WRITE (*,*) 'NO OF FREQ. TO CONVERT, 1 OR 2  '
      READ(*,*) IJ
      IF (IJ .GT. 2) GOTO 200
      OA = 2 * PI
      DO 210 I = 1 , IJ
      WRITE (*,*) 'FREQ. IN Hz    '
      READ(*,*) OHZ(I)
      OR(I) = OHZ(I) * OA/1E9
  210 CONTINUE
      WRITE (*,*) '   HZ(1)        R/nsec      HZ(2)       R/nsec '
      WRITE (*,*) OHZ(1),OR(1),OHZ(2),OR(2)
      RETURN
      END
C
C                        EXPONENTIAL TAIL ROUTINE
C*****************************************************************
C*****************************************************************
C
      SUBROUTINE EXPONT(RDIF,NPDIF,NP,NPS,TI,BETA,TAU)
      IMPLICIT REAL * 8 (A-H)
      IMPLICIT REAL * 8 (O-Z)
      REAL * 4 RDIF(1024),BETA,TAU,TI
      DIMENSION DIF(1024),TM(1024),C(1024)
      SAVE
C
C         Y = B * EXP(-t / TAU)
C
C         WHERE Y = POSITION ON SCREEN AT TIME = t
C               TAU = TIME CONSTANT FOR EXPONTIAL DECAY OF THE
C                     END OF THE DIFFERENCE CURVE.
C
      WRITE (*,*) ' NUMBER OF PTS. FROM END OF DIF. CURVE THAT WILL'
      WRITE (*,*) ' BE USED TO FIND TAU AND BETA.'
      READ (*,*) NPDIF
      WRITE (*,*) '                '
      WRITE (*,*) ' WISH TO DOUBLE (2), OR TRIPLE (3) TIME WINDOW, OR'
      WRITE (*,*) ' LENTHEN THE CURVE BY THE NO. OF PTS. ENTER HERE'
      READ (*,*) SIZE
      IF (SIZE .EQ. 2) THEN
           NPS = 2 * NP
      ELSE IF (SIZE .EQ. 3) THEN
           NPS = 3 * NP
      ELSE
           NPS = SIZE + NP
      END IF
      DO 70 K = 1,NP
   70      DIF(K) = DBLE(RDIF(K))
C
      NPD1 = NP - NPDIF
      L = NPD2
```

```
      DATA TWO, QUART, HALF/2.0, .25, 0.5/
      IST = NP - 2
      L01 = L + 1
      L02 = L + 2
      NP1 = NP - 1
        DO 90 K = 1 , 2
           A1=DIF(L)
           A2=DIF(L01)
           DQ=A1+ TWO *A2+DIF(L02)
           DO 100 J = L01 , IST
              J1 = J + 1
              J2 = J + 2
              DIF(J)  = QUART * DQ
              DQ=DQ+DIF(J1)+DIF(J2)-A1-A2
              A1=A2
              A2=DIF(J1)
 100       CONTINUE
           DIF(NP1) = QUART * DQ
           DIF(NPR) = HALF * (A2 + DIF(NPR))
           DIF(L)  = HALF * (DIF(L)  + DIF(L01))
 90     CONTINUE
      SMALL = DIF(1)
      DO 2960 K = 2,NP
         IF (DIF(K) .LT. SMALL) SMALL = DIF(K)
 2960 CONTINUE
      WRITE (*,*) '       '
C
      TI1 = DBLE(TI)
      DO 3000 K = NPD2,NP
         TM(K) = TI1 * DBLE(K)
      DO 3020 K = NPD2,NP
         IF (SMALL .LT. 0) DIF(K) = DIF(K) - SMALL
 3020    C(K) = LOG(DIF(K))
C
      CALL LLS(C,TM,BETA,TAU,NP,NPDIF)
C
      RETURN
      END
C
C                              LLS ROUTINE
C*****************************************************************
C*****************************************************************
C
      SUBROUTINE LLS(E1,A,BETA,TAU,NP,NPDIF)
      IMPLICIT REAL * 8 (A-H)
      IMPLICIT REAL * 8 (O-Z)
      REAL * 4 BETA,TAU,A01,A11,D01,D11,D1
      DIMENSION E1(1024),A(1024),W(1024)
      SAVE
C
C     PROGRAM FROM Wilkins,Klopfenstein,Isenhour and Jurs, INTRODUCTION
C      TO COMPUTER PROGRAMMING FOR CHEMISTS  BASIC VERSION (1974) p.301
C
      DATA S2, D0, D1/0.,0.,0./
 5980 WRITE(*,*) 'WEGHTING OF DATA: UNIT(1) OR INVERSE(2)  :'
      WRITE(*,*) 'DEFAULT = UNIT    '
      READ(*,*) N9
      IF (N9 .EQ. 0) N9 = 1
      IF ((N9 .NE. 1) .AND. (N9 .NE. 2)) GOTO 5980
      ONE = 1.
      NPD2 = NP - NPDIF
      DO 4220 J = NPD2,NP
         IF (N9 .EQ. 1) THEN
               W(J) = ONE
         ELSE
               W(J) =  ONE / E1(J)
         END IF
 4220 CONTINUE
C
C     SUMMATION ROUTINE, THEN PRINT ROUTINE
      GOTO  7780
C
 4230 RETURN
C**********************    PRINT ROUTINE  ***************************
 7000 WRITE(*,*)'     '
```

```
      WRITE(*,*)'     '
      M = NPDIF
      IXX  = 1/A1
      BETA = REAL(EXP(A0))
      TAU  = REAL(-IXX)
      A01 = REAL(A0)
      A11 = REAL(A1)
      D01 = REAL(D0)
      D11 = REAL(D1)
      D1  = REAL(D)
      WRITE(*,*) 'INTERCEPT    ',A01,'   STD DEV    ',D01
      WRITE(*,*) '     '
      WRITE(*,*) 'SLOPE    ',A11,'   STD DEV    ',D11
      WRITE(*,*) '     '
      WRITE(*,*) '1/SLOPE    ',REAL(IXX)
      WRITE(*,*) '     '
      WRITE(*,*) 'OVERALL STD DEV    ',D1,'  BASED ON    ',M,'   DATA POINTS'
      WRITE(*,*)'     '
      WRITE(*,*)'     '
      WRITE(*,*)' DO YOU WISH A TABLE (1 = YES)   :'
      READ(*,*) Y
      IF (Y .NE. 1 ) GOTO 6230
      WRITE(*,*)'     '
      WRITE(*,*)'     '
 7620 WRITE(*,*)'POINT #     ',' X VALUE     ','Y VALUE     ','
     * WEIGHT     ','CALC. Y VALUE'
      WRITE(*,*)'     '
      WRITE(*,*)'     '
      DO 7700 J = NPD1, NP
         WRITE(*,*) REAL(J),REAL(A(J)),REAL(E1(J)),REAL(W(J)),
     *REAL(A0+A1*A(J))
 7700 CONTINUE
      GOTO 6230
C
C*********************  SUMMATION ROUTINE  *********************
 7780 DATA Z0, Z1, Z2, Z3, Z4, Z5/0.,0.,0.,0.,0.,0./
      DATA A0, A1, Q, D/0.,0.,0.,0./
C     A(J)   = X COORDINATES
C     E1(J)  = Y COORDINATES
      DO 7960 J = NPD1, NP
         Z0 = Z0 + W(J)
         Z1 = Z1 + W(J) * A(J)
         Z2 = Z2 + W(J) * E1(J)
         Z3 = Z3 + W(J) * A(J) * E1(J)
         Z4 = Z4 + W(J) * A(J) * A(J)
         Z5 = Z5 + W(J) * E1(J) * E1(J)
 7960 CONTINUE
      D  = Z0 * Z4 - Z1 * Z1
      A0 = (Z4 * Z2 - Z1 * Z3) / D
      A1 = (Z0 * Z3 - Z1 * Z2) / D
      Q  = 0.
      DO 8100 J = NPD1, NP
         Q = Q + W(J) * (E1(J) - A0 - A1 * A(J)) ** 2
 8100 CONTINUE
C     NOTE NP -2 METHOD
      S2 = Q / REAL(NP -2)
      D0 = SQRT(S2 * Z4 / D)
      D1 = SQRT(S2 * Z0 / D)
      D  = SQRT(S2)
      GOTO 7000
      END
C
C                    ADDING TAIL TO DIF. ARRAY
C*****************************************************************
C*****************************************************************
      SUBROUTINE TAIL(DIF,NPS,NP,BETA,TAU,TI)
      REAL * 8, TA,B,TI1,TMT,D
      DIMENSION DIF(3072)
      SAVE
C
      TA = DBLE(TAU)
      B  = DBLE(BETA)
      TI1 = DBLE(TI)
      DO 3040 K = NP,NPS
         TMT = - TI1 * DBLE(K) / TA
```

```
            D = B * EIP(TMT)
 3040       DIF(K) = REAL(D)
        RETURN
        END
C                   SENDING SUM AND DIFF TO DISK
C*****************************************************************
C*****************************************************************
        SUBROUTINE SENC(NPR,VCRD,HCRD,DIF,B,TAU)
        REAL * 4 DIF(3047),HCRD
        CHARACTER *15 PS
        SAVE
 1000   PRINT *, 'ENTER NAME OF DIFF. OR REF. FILE, ADD QUOTATION MARKS'
        READ (*,*) PS
        IF (B .NE. 0) THEN
            WRITE (*,*) 'SENDING DIF. WITH TAIL TO DISK'
            OPEN (8,FILE = PS,STATUS = 'NEW',ERR = 1000)
            WRITE (*,*) ' NO. OF PTS  ',NPR
            WRITE (8,*) NPR
            WRITE (8,*) VCRD
            WRITE (8,*) HCRD
            DO 135 J = 1 , NPR
                WRITE(8,*) DIF(J)
  135       CONTINUE
            WRITE (8,*) B
            WRITE (8,*) TAU
            CLOSE (8)
        ELSE
            OPEN (4,FILE = PS,STATUS = 'NEW',ERR = 1000)
            WRITE (*,*) '  SENDING DIFF ARRAY TO DISK'
            WRITE (4,*) NPR
            WRITE (4,*) VCRD
            WRITE (4,*) HCRD
            DO 130 J = 1 , NPR
                WRITE(4,*) DIF(J)
  130       CONTINUE
            CLOSE (4)
        END IF
        RETURN
        END
```

APPENDIX D
COMPUTER PROGRAMS USED TO INTERFACE THE IBM CS-9000 COMPUTER WITH THE TEKTRONIX 7854 DIGITIZING OSCILLOSCOPE

TEKSEND2.BAS..... 242

TEKEX13.BAS..... 245

The program titled TEKSEND2.BAS and TEKEX13.BAS are used to acquired the reference and sample time domain data from the TEKTRONIX 7854 Digitizing Oscilloscope. The program titled TEKEX13.BAS is a generalized interface program.

```
5 REM PROGRAM TEKSEND.BAS
6 REM DERIVED DIRECTLY FROM PROGRAM TEKBPT13
7 REM THIS PROGRAM HAS SUB 1292, which sends LF,SP,DEL,CR.  ALSO CHANGE
8 REM FUNC. PACKAGE LINE 190-200 (EOS = LF) NOT (CR).
10 REM PROGRAM TEKBPT10  With serail poll disable fuction (30) modified 2/28/83
30 REM     SEE EXAMPLE PROGRAM p. 15-19 IN DOS 1.0 BASIC MANUAL
40 REM     ALSO SEE IEEE IN BASIC 1.1 and PART II FOR FUNCTION PACKAGE
50 REM     ALSO SEE p. 2-7 IN BASIC 1.0 REFERENCE MANUAL
60 PRINT"THIS PROGRAM IS COMBINED FROM TEK488N AND TEKOBJ,  THEN DERIVED FROM"
70 PRINT "TEKBTS"
80 DIM F%(55),Y(1024)
90 DIM P$(200),A$(50),B%(8200),D$(1024)
100 B$="EXIT"
110 C$="WFMPRE"
120 OPEN "#BUSC?" AS FILE #6
130 F%(1)=42                    !SET OPTIONS                    !
140 F%(2)=17                                                    !
150 F%(3)=30                    !TIMEOUT = ABOUT 13 MIN         !
160 F%(4)=500                                                   !
170 F%(5)=43                    !NF?                            !
180 F%(6)=-1                                                    !   FUNCTION F%(1)
190 F%(7)=32                    !EOS =LF                        !
200 F%(8)=10                                                    !
210 F%(9)=45                    !NR?                            !
220 F%(10)=-1                                                   !
240 F%(32)=21                   !SERIAL POLL ENABLE             !
241 F%(37)=28
250 F%(12)=0     !XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
280 F%(21)=27                   !SEND SERIAL POLL
290 F%(22)=%433F
300 F%(23)=-1
310 F%(24)=%3F3F
320 F%(25)=0      !XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
330 F%(30)=20                   ! SERIAL POLL DISABLE
340 F%(31)=0      !XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
350 F%(35) = 2                  !SEND DEVICE CLRAR AND UNLISTEN
360 F%(36) = 0
400 CALL SYSFUNC(6,F%(1))
450 GO SUB 1230
451 GO SUB 1300
452 INPUT "P/W; HCRD(nsec); VCRD(mV)    :";PT,HCRD,VCRD
455 FOR MM = 1 TO 2
460 GOSUB 1100
465 GOSUB 505
470 NEXT MM
475 CLOSE #6
480 STOP
505 REM SUBROUTINE TO BRING DATA OVER
507 IF MM = 1 THEN A$ = "2 WFM SENDI"
508 IF MM = 2 THEN A$ = "3 WFM SENDI"
530 PRINT #6,A$;        ! SEND MESSAGE TO DEVICE; NO ADDED (CR)
540 PRINT "SENT: ",A$,":"
550 INPUT LINE #6,P$                    ! TEK7854 TO IEEE-BUFFER
553 GOSUB 1292
555 CALL SREAD (6,B%(1),8200.,13,13,0.)
557 CALL SYSFUNC(6,F%(35))
560 PRINT P$
570 Z$=MID(P$,2,6):W$=MID(C$,1,6)       ! CHECK TO SEE IF  WFM
590 PRINT Z$,W$                         ! HAS COME OVER OR IF DATA
640 LENG = 8 * PT + 6
645 PRINT"                      DATA CONVERSION IN PROCESS"
649 REM
670 DATA$ = "" : LENG% = INT(LENG/2) - 1 : JJ% = 0 : E$ = ""
672 FOR J% = 1 TO 3                     ! LOOP TO REMOVE 'CURVE '
674 E$ = E$ + CVT%$(B%(J%))
676 NEXT J%
678 REM
680 FLAG% = 1 : KK% = 1
682 FOR J% = 4 TO LENG%
684 KK% = KK% + 1
686 E% = B%(J%)
688 C% = (E% AND $00FF)
690 IF C% = 44 GOTO 704
```

```
692 C% = (SWAP%(E%) AND $00FF)
694 IF C% = 44 GOTO 732
696 DATA$ = DATA$ + CVT%$(B%(J%))
698 GOTO  752
700 REM              END LOOP TO FIND `,'
702 REM
704 JJ% = JJ% + 1
706 IF (FLAG% = 1) GOTO 718
708 F% = J% - KK%
710 A% = B%(F%)
712 D% = (A%) AND $00FF
714 DATA$ = CHR$(D%) + DATA$
716 REM
718 D% = (SWAP%(E%)  AND $00FF)
720 DATA$ = DATA$  + CHR$(D%)
722 Y(JJ%) = VAL(DATA$)
724 FLAG% = 1
726 GOTO 750
728 REM
730 REM
732 IF (FLAG% = 1) GOTO 742
734 F% = J% - KK%
736 A% = B%(F%)
738 D% = (A%) AND $00FF
740 DATA$ = CHR$(D%) + DATA$
742 JJ% = JJ% + 1
744 FLAG% = 2 :KK% = 0
746 Y(JJ%) = VAL(DATA$)
748 REM GOTO 752  !WITH UPGRADE DON'T NEED THIS ANY MORE
750 DATA$ = ""
752 NEXT J%
754 Y(PT) = Y(PT-1)
756 C% = INT(LENG / 8)
758 PRINT    "
822 IF MM = 1 THEN SA = 0
823 IF MM = 2 THEN SA = 1
824 IF SA() 0 GOTO 835
830 OPEN "REFD011.DAT" FOR OUTPUT AS FILE #1
833 GOTO 837
835 OPEN "SAMD010.DAT" FOR OUTPUT AS FILE # 1
837 PRINT #1,PT                    ! NO. OF DATA PT.
838 PRINT #1,VCRD
839 PRINT #1,HCRD
840 FOR J% = 1 TO C%
845 ON ERROR GOTO 900
850 PRINT #1, Y(J%)
870 NEXT J%
900 CLOSE #1
910 PRINT"******************** DONE $$$$$$$$$$$$$$$       "
925 RETURN
1090 REM ************************************************
1100 REM ROUTINE TO PROCESS DATA WHICH IS NOT WFM DATA
1110 CALL SYSFUNC(6,F%(1))
1120 IF MM = 1  THEN A$ = "2 WFM"
1130 IF MM = 2 THEN A$ = "3 WFM"
1150 PRINT #6,A$;
1160 PRINT "SENT:  ",A$,"."
1180 INPUT LINE #6,P$
1190 PRINT P$
1200 GOSUB 1230
1201 IF MM = 2 GOTO 1210
1202 PRINT #6,A$;
1203 PRINT "SENT:  ",A$,"."
1204 INPUT LINE #6,P$
1205 PRINT P$
1206 GOSUB 1230
1210 RETURN
1220 CLOSE #6
1230 REM SUBROUTINE TO GET STATUS BITE
1240 CALL SYSFUNC(6,F%(21))
1270 PRINT "STATUS BITE FROM SCOPE:":PRINT F%(23)
1280 RETURN
1292 PRINT#6,CHR$(10):PRINT#6,CHR$(32):PRINT#6,CHR$(127)
1293 PRINT#6,CHR$(13)
1294 RETURN
```

```
1300 REM ************************************************************
1310 REM SENDING SCOPE AND STORED TO TEK-SCOPE TO CLEAR BUS
1320 FOR M% = 1 TO 3
1325       CALL SYSFUNC(6,F%(1))
1330       IF (M% = 3) THEN A$ = 'STORED' ELSE A$ = 'SCOPE'
1340       PRINT @6, A$
1350       PRINT "SENT:    ",A$,"."
1360       INPUT LINE @6,P$
1370       PRINT P$
1380       CALL SYSFUNC(6,F%(21))
1385       PRINT "STATUS BITE FROM SCOPE:":PRINT F%(23)
1386!         SINE LOOP FOR DELAY
1387       FOR I = 1 TO 100:X = SIN (I)
1388       NEXT I
1390 NEXT M%
1400 RETURN
1410 END
```

```
70 REM                              TEKEX13.BAS
71 REM                          BY ERNEST F. STINE JR.
72 REM                                1/9/87
75 REM
76 REM    PROGRAM CONTROLS THE  TEKTRONIX 7854 OSCILLOSCOPE
77 REM
78 REM IF THE PARALLEL PORT ON THE CS-9000 IS OPEN AND CLOSED WHILE IN BASIC,
79 REM THEN SYSTEM IS RETURNED TO THE OPERATING SYSTEM .LOAD BASIC AND OPEN
80 REM THE PORT AGAIN.  THE CS-9000 WILL OFTEN SEND A SERVICE REQUEST AT THAT
81 REM TIME OR SOON AFTERWARDS OVER THROUGH THE PORT.
100 DIM Y(1028),IN(1028)
110 REM PROGRAM TEKBPT13
120 REM THIS PROGRAM HAS SUB 1560, which sends LF,SP,DEL,CR. ALSO CHANGE
130 REM FUNC. PACKAGE LINE 190-200 (EOS = LF) NOT (CR).
150REM PROGRAM TEKBPT10 With serail poll disable fuction (30) modified 2/28/33
160 REM     SEE EXAMPLE PROGRAM p. 15-19 IN DOS 1.0 BASIC MANUAL
170 REM     ALSO SEE IEEE IN BASIC 1.1 and PART II FOR FUNCTION PACKAGE
180 REM     ALSO SEE p. 2-7  IN BASIC 1.0 REFERENCE MANUAL
190 PRINT"THIS PROGRAM IS COMBINED FROM TEK488N AND TEKOBJ,  THEN DERIVED FROM"
200 PRINT "TEKBT5.BAS"
210 DIM F%(55)
220 DIM P$(200),A$(50),B%(8200)
230 B$="EXIT"
240 C$="WFMPRE"
250 OPEN "#BUSC?" AS FILE #6
260 F%(1)=42                    !SET OPTIONS                    !
270 F%(2)=17                                                    !
280 F% 3)=30                    !TIMEOUT = ABOUT 5  SEC         !
290 F%(4)=100                                                   !
300 F%(5)=43                    !NF?                            !
310 F%(6)=-1                                                    !   FUNCTION F%(1)
320 F%(7)=32                    !EOS =LF                        !
330 F%(8)=10                                                    !
340 F%(9)=45                    !NR?                            !
350 F%(10)=-1                                                   !
360 F%(32)=21                   !SERIAL POLL ENABLE             !
370 F%(37)=28
372 F%(38)=290          ! SET DMA (DIRECT MEMORY ACCESS)
373 F%(39)=1
380 F%(12)=0      !XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
390 F%(21)=27                   !SEND SERIAL POLL
400 F%(22)=&H33F
410 F%(23)=-1
420 F%(24)=&H3F3F
430 F%(25)=0        !XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
440 F%(30)=20               ! SERIAL POLL DISABLE
450 F%(31)=0        !XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
460 F%(35) = 2              !SEND DEVICE CLRAR AND UNLISTEN
470 F%(36) = 0
480 CALL SYSFUNC(6,F%(1))
490 GO SUB 1580
500 PRINT"*********    WFM ENTER (2), OTHER DATA(1)    ******** "
510 INPUT J
515 IF (J ( 1) OR (J ) 2) GOTO 500
520 IF J = 1 GOTO 1350
530 PRINT "TO EXIT FROM PROGRAM ENTER (EXIT) AS MESSAGE"
540 PRINT "ENTER MESSAGE TO SEND TO TEKSCOPE"
550 INPUT LINE A$                   ! INPUT FROM @CON TO IBM
560 IF MID(A$,1,4)=MID(B$,1,4) GOTO 1540
570 PRINT #6,A$;      ! SEND MESSAGE TO DEVICE; NO ADDED (CR)
580 PRINT "SENT: ",A$,""
590 INPUT LINE #6,P$                ! TEK7854 TO IEEE-BUFFER
600 GOSUB 1560
610 CALL SREAD (6,B%(1),8200.,13,13,0.)
620 CALL SYSFUNC(6,F%(35))
630 PRINT P$
640 Z$=MID(P$,2,6):W$=MID(C$,1,6)       ! CHECK TO SEE IF  WFM
650 PRINT Z$,W$                         ! HAS COME OVER OR IF DATA
670 INPUT "P/W" ; INPUT PT : LENG = 8 * PT + 6
675 INPUT "HCRD(nsec); VCRD(mV)   :";HCRD,VCRD
680 DATA$ = "" : LENG% = INT(LENG/2) + 1 : JJ% = 0 : E$ = ""
690 FOR J% = 1 TO 3                     !  LOOP TO REMOVE `CURVE '
700 E$ = E$ + CVT%$(B%(J%))
```

```
710 NEXT J%
715 REM
719 FLAG% = 1 : KK% = 1:JJ% = 0
720 FOR J% = 4 TO LENG%
725 KK% = KK% + 1
730 E% = B%(J%)
750 C% = (E% AND $00FF)
770 IF C% = 44 GOTO 850
780 C% = (SWAP%(E%) AND $00FF)
800 IF C% = 44 GOTO 960
820 DATA$ = DATA$ + CVT%$(B%(J%))
840 GOTO 1020
845 REM
844 REM                END LOOP TO FIND ','
850 JJ% = JJ% + 1
852 IF (FLAG% = 1) GOTO 880
854 F% = J% - KK%
856 A% = B%(F%)
858 D% = (A%) AND $00FF
859 DATA$ = CHR$(D%) + DATA$
860 REM
880 D% = (SWAP%(E%)  AND $00FF)
890 DATA$ = DATA$  + CHR$(D%)
900 Y(JJ%) = VAL(DATA$)
905 FLAG% = 1
910 GOTO 1010
915 REM
916 REM
960 IF (FLAG% = 1) GOTO 970
962 F% = J% - KK%
965 A% = B%(F%)
967 D% = (A%) AND $00FF
969 DATA$ = CHR$(D%) + DATA$
970 JJ% = JJ% + 1
975 FLAG% = 2 :KK% = 0
990 Y(JJ%) = VAL(DATA$)
1005 REM GOTO 1020    !WITH UPGRADE DON'T NEED THIS ANY MORE.
1010 DATA$ = ""
1020 NEXT J%
1023 Y(PT) = Y(PT-1)
1024 C% = INT(LENG / 8)
1025 RESTORE
1026 PRINT     "     "
1030 INPUT" NAME OF FILE WITHOUT EXT."NAME$
1035 IF (NAME$ = "") THEN GOTO 1030
1036 NAME$ = NAME$ + '.DAT'
1050 OPEN NAME$ FOR OUTPUT AS FILE #1
1075 PRINT #1, PT
1076 PRINT #1, VCRD
1077 PRINT #1, HCRD
1080 FOR JJ% = 1 TO C%
1090 ON ERROR GOTO 1120
1100 PRINT #1, Y(JJ%)
1110 NEXT JJ%
1120 CLOSE #1
1130 PRINT"********************* DONE $$$$$$$$$$$$$$$          "
1140 INPUT" DO YOU WISH TO SEE THE DATA, 1=YES     ";SB
1150 IF SB <> 1 GOTO 1330
1200 OPEN NAME$ FOR INPUT AS FILE #2
1220 FOR J% = 1 TO C%
1230 ON ERROR GOTO 1252
1240 INPUT #2,IN(J%)
1250 NEXT J%
1251 GOTO 1255
1252 PRINT "ERROR IN RECEIVING DATA FROM DISK"
1255 CLOSE #2
1260 FOR J% = 1 TO C%
1270 PRINT IN(J%)
1280 NEXT J%
1300!CALL SYSFUNC(4,F%(30))        !SEND S. POLL  TO BREAK 'BUSY' ON SCOPE
1310!CALL SYSFUNC(4,F%(35))        !SEND DEVICE CLEAR AND UNLISTEN
1320 GOSUB 1480
1325 NAME$ = ""
1330 GOTO 500
1340 REM ************************************************
```

```
1350 REM ROUTINE TO PROCESS DATA WHICH IS NOT WFM DATA
1360 CALL SYSFUNC(6,F%(1))
1370 PRINT "ENTER MESSAGE TO SCOPE     "
1380 INPUT LINE A$
1390 IF MID(A$,1,4) = MID(B$,1,4) GOTO 1540
1400 PRINT #6,A$;
1410 PRINT "SENT:  ",A$,"."
1420 INPUT LINE #6,P$
1430 PRINT P$
1440!CALL SYSFUNC(6,F%(35))
1450 GOSUB 1480
1460 GOTO 500
1470 CLOSE #6
1480 REM SUBROUTINE TO GET STATUS BITE
1490 CALL SYSFUNC(6,F%(21))
1500 PRINT"0=NORMAL, 2=EXT.COMMAND COMPLETE, 34=ERROR, 80=RQS, 146=SENDI"
1510 PRINT"147=READI"
1520 PRINT "STATUS BITE FROM SCOPE:":PRINT F%(23)
1530 RETURN
1540 CLOSE #6
1550 STOP
1560 PRINT#6,CHR$(10):PRINT#6,CHR$(32):PRINT#6,CHR$(127)
1570 PRINT#6,CHR$(13)
1580 RETURN
1590 END
```

APPENDIX E
COMPUTER PROGRAMS USED TO GRAPH THE TIME DOMAIN AND FREQUENCY DOMAIN DATA

GRSCOPE2.BAS..... 249

GRAPH7D.BAS..... 252

The program titled GRSCOPE2.BAS graphs the time domain data. The program titled GRAPH7D.BAS graphs the frequency domain data and calculates the critical frequency of the sample.

```
70   REM                    PROGRAM GRSCOPE3.BAS
71   REM                    BY ERNEST F. STINE JR.
72   REM                          1/9/85
75   REM            THIS PROGRAM GRAPHS TIME DOMAIN DATA
76   REM
77   REM REFD011.DAT AND SAMD010.DAT ARE FROM: TEKEX13.BAS OR TEKSEND.BAS
78   REM (CS-9000).
79   REM OUT.TIT AND CTIME.TXT ARE FILES FROM THE "INVERSE.FOR" SERIES.  AT
80   REM THE PRESENT, IT IS BEST TO RENAME YOUR DATA FILE FROM "INVD3.FOR"
81   REM (VAX) TO CTIME.TIT (CS-9000).
82   REM ANY FILES BESIDES THE INVERSE.FOR SERIES FILES CAN BE USED BY
83   REM USING SELECTION #5-- LINE 210
84   REM SELECTION #4, DIFFERENCE SPECTRUM, IS FOR CURVES WITHOUT TIME
85   REM SHIFTING.  TO GET AN INTEGRAL NUMBER OF PTS. TIME SHIFTED AS WOULD
86   REM BE DONE IN "KDSAM9E.FOR" (VAX), USE "DIFFER.FOR" (CS-9000), THEN
87   REM USE SELECTION #5-- LINE 220.
88   REM
89   REM     PW   = NO. OF PTS. IN WAVEFORM
90   REM     VCRD = VERTICAL SCALE ON SCOPE
91   REM     HCRD = HORIZONTAL SCALE ON SCOPE
92   REM
93   REM THE WAVEFORM CAN BE (1) EXPANDED VERTICALLY OR HORIZONTALLY: SC1,SC2
94   REM (2) SHIFTED TO RT. OR LEFT ON SCREEN "X AXIS POSITION": XP%
95   REM (3) MAY FIND A PT. BY USING "DESIRE TO MARK A PT.?": POINT.  THIS
96   REM IS USEFUL TO DECIDE WHERE TO START THE EXPONENTIAL DECAY FUNCTION
97   REM WHEN ADDING " A + EXP(-1/TAU) " TAIL TO THE WAVEFORM.
98   REM (4) MAY FIND A MIN. VALUE BY USING "WISH PT. POSITION PRINTED OUT?":
99   REM PROUT, EG. FIND TIMEING MARKER POSITION.
100  REM
120  CLS
140  ON ERROR GOTO 2140
160  REM PLOT OF SAMD010.DAT, REFD011.DAT, OR OUT.TIT
180  DIM X(1025),Y(1025),R(1024),S(1024)
200  PRINT "REFD011.DAT(1); SAMD010.DAT(2); OUT.TIT(3); CTIME.TIT(4)    :"
220  INPUT "          FILENAME(5); DIFFERENCE(6); QUIT(7)     :";A%
240  IF (A% ( 1) OR (A% ) 7) GOTO 200
260  IF (A% = 6) GOTO 2260
280  IF (A% = 5) THEN INPUT "FILENAME OF CMP (WITHOUT EXT)   ";P$
300  P$ = P$ + '.DAT'
320  IF (A% = 1) THEN P$ = 'REFD011.DAT'
340  IF (A% = 2) THEN P$ = 'SAMD010.DAT'
360  IF (A% = 3) THEN P$ = 'OUT.TIT'
380  IF (A% = 4) THEN P$ = 'CTIME.TIT'
400  IF (A% = 7) GOTO 2640
420  OPEN P$ AS FILE #3
440  IF (A% = 3) GOTO 740      !************************************
460  IF (A% = 4) GOTO 660
480       INPUT #3,PW
500       INPUT #3,VCRD
520       INPUT #3,HCRD
540  PW% = PW
560  FOR I% = 1% TO PW%
580       INPUT #3,Y(I%)
600  NEXT I%
620  CLOSE #3
640  GOTO 740
660  INPUT "PW    ";PW
680  PW% = PW
700  INPUT "HCRD    ";HCRD
720  GOTO 820
740  REM A = TOTAL TIME OF SPECT. IN msec. ; B = TIME INTERVAL; PW = # TIME PT.
760       INPUT #3,A,B,PW
780  PW% = PW
800  HCRD = A/10
820  FOR I% = 1% TO PW%   STEP 4
840       ON ERROR GOTO 920
860       INPUT #3,Y(I%),Y(I%+1),Y(I%+2),Y(I%+3)
900  NEXT I%
920  CLOSE #3
940  HPW% = PW / 2
960  L = Y(1)
```

```
980 FOR I% = 1% TO HPV%
1000      IF (Y(I%) ( L) THEN L = Y(I%)
1020 NEXT I%
1040 TI = HCRD * 10 / PV
1060 IF (A% = 3) THEN TI = 8
1080 X(1) = 0
1085 REM THE SCREEN ONLY GRAPHS POSITIVE VALUES, THUS ALL VAUES SHIFTED
1086 REM "UP" BY "L"
1100 FOR I% = 1% TO PV%
1120      Y(I%) = Y(I%) - L
1140      X(I% + 1) = I% * TI
1180 NEXT I%
1200 REM TRY: FOR 2 NSEC. WINDOW SET SC1 TO 350, 140 FOR 10,5  NSEC.
1220 SC2 = 60
1240 IF (A%=4) THEN SC2 = 320
1260 IF (A%=3) THEN SC2 = 10
1280 INPUT " X COORDINATE EXPANSION FACTOR (SC1)  ";SC1
1300 PRINT " Y COORDINATE EXPANSION FACTOR (SC2), (CR) FOR DEFAULT  "
1320 PRINT "      PRESENT EXPANSION FACTOR = ";SC2:INPUT YEXP
1340 IF (YEXP () 0) THEN SC2 = YEXP
1360 INPUT " X AXIS POSITION, (CR) FOR DEFAULT = 20  ";XP%
1380 IF (XP% = 0) THEN XP% = 20%
1385 INPUT "DESIRE TO MARK A POINT ? IF SO ENTER ITS POSITION",POINT
1400 INPUT"WISH PT.  POSITION PRINTED OUT; 1 = Y  ";PROUT
1420 IF (PROUT () 1) GOTO 1500
1440 INPUT "FIRST AND LAST PT. OF PRINT OUT  ";FIRST,LAST
1460 INPUT "WISH TO FIND MIN. PT?  1 = Y ";MINNO
1480 FI% = FIRST - 1:LA% = LAST + 1:B = Y(FI%):MP% = 1
1500 CLS
1520 F% = 50%:IT = .009
1524 IPS% = 2%
1525 IF XP% ( 0 THEN XP5% = -XP%
1540 FOR I% = XP5% TO PV%
1560      XI = X(I%): XX = INT(XI)
1580      LINE(SC1*X(I%-1)+XP%,SC2*Y(I%-1)+F%,SC1*XI+XP%,SC2*Y(I%)+F%)
1600      IF (I% ) LA%) GOTO 1740
1620      IF (PROUT () 1) GOTO 1760
1640      I$ = NUM$(I%)
1660      IF I% )FI% THEN TEXT(350,415,I$)
1680      IF (MINNO () 1) THEN GOTO 1760
1700      IF (FI% ) I%) GOTO 1740
1720           IF Y(I%) )= B GOTO 1740 ELSE B = Y(I%)
1740           MP% = I%
1760      IF ((XX - IT) (= XI) AND ((XX + IT) )= XI) GOTO 1800
1780      GOTO 1840
1800      X$ = NUM$(XI):X$ = LEFT$(X$,6)
1820      TEXT(SC1*X(I%-1)+XP%,20,X$)
1840 NEXT I%
1842 IF (POINT = 0) GOTO 1860
1844 TEXT (SC1 * X(POINT)+13,SC2 * Y(POINT)+F%,"*")
1846 TEXT(20,400,"MARK ANOTHER POINT? ENTER ITS POSITION"):INPUT POINT
1848 IF (POINT () 0) GOTO 1844
1860 B$ = NUM$(MP%): XI$ = NUM$(X(MP%)): MP% = 1
1880 IF (MINNO = 1) THEN TEXT(350,415,"MIN = "+B$ + ", " + XI$ + " msec.")
1900 MINNO = 0
1920 SC1$ = NUM$(SC1) + ' ':SC2$ = NUM$(SC2) + ' ':IP$ = NUM$(XP%)
1940 TIM$ = DATE$ + '    ' + TIME$:SCA$ = 'SCALING: '+SC1$+SC2$+IP$
1960 TEXT (50,415,'DATE    ' + TIM$) :TEXT (50,430,F$+ '    ' + SCA$)
1980 REM  WHEN THE CS #000 WAS UPGRADED TO 1.3, AT TIMES IT WOULD NO LONGER
2000 REM  PRINT WHILE THE TIME LOOP (LINE 2820) WAS IN PROGRESS.  USE "INPUT
2020 REM  START" TO HOLD GRAPH WHILE DUMPING SCREEN.
2040 ! INPUT START
2060 FOR I = 1 TO IE4:NEXT I
2080 INPUT "WISH TO REPEAT ,Y = YES  (DEFAULT = NO)  ";A$
2100 IF (A$ = 'Y') GOTO 1200
2120 GOTO 140
2140 PRINT " ERROR ENCONTERED"
2160 CLOSE #3
2180 STOP
2200 REM ************************************6666666666666**********************************
2220 REM ************************************************************************
2240 REM ROUTINE TO OBTAIN DIFFERENCE SPECTRUM
2260 INPUT "FILENAME OF REFERENCE (WITHOUT EXT.)    ";R$:R$ = R$ + '.DAT'
2280 INPUT "FILENAME OF SAMPLE (WITHOUT EXT.)       ";S$:S$ = S$ + '.DAT'
2300 FOR J% = 1% TO 2%
```

```
2320        IF (J% = 1%) THEN OPEN R$ AS FILE #3
2340        IF (J% = 2%) THEN OPEN S$ AS FILE #3
2360        INPUT #3,PW
2380        INPUT #3,VCRD
2400        INPUT #3,HCRD
2420        PW% = PW
2440        FOR I% = 1% TO PW%
2460              IF (J% = 1%) THEN INPUT #3,R(I%)
2480              IF (J% = 2%) THEN INPUT #3,S(I%)
2500        NEXT I%
2520        CLOSE #3
2540 NEXT J%
2560 FOR I% = 1% TO PW%
2580        Y(I%) = R(I%) - S(I%)
2600 NEXT I%
2620 GOTO 940
2640 CLOSE #3
2660 END
```

```
100 !                          GRAPH7C.BAS
120 !                      ERNEST F. STINE JR.
140 !                           11/4/84
160 !
180 ! E1()     REAL COMPONENT OF EPS; FROM DSAMT6 OR DSAMT7 PROGRAM
200 ! E2()     IMAG. COMPONENT
220 ! FR()     ANGULAR FREQ. IN RADIANS PER nsec.
240 ! F()      FREQ. IN GHz.
260 ! E3()     INITIALLY SAME AS F(), CHANGED TO Ln(E3())    "IN MHz."
280 ! W()      WEIGHTING FACTOR IN LINEAR LEAST SQ. PROGRAM
300 !     INPUT IS FROM:
320 !          FREP015.DAT
340 !          FREP   .DAT   (FREP015.DAT MODIFIED WITH EXPONENTIAL TAIL)
360 !     OUTPUT IS TO:
380 !          GRAPH5U8.DAT  (LAYOUT FOR E1() VS E3())
400 !          GRAPH5U1.DAT  (LAYOUT FOR E2() VS E3())
420 CLS
440 TEXT(300,300,"GRAPH7",4)
460 TEXT(250,200,"FOR TDR",3)
480 X% = 767
500 Y% = 479
520 DIM FPK%(22)
540 FPK%(1)=21
560 FPK%(2)=0
580 FPK%(3)=0
600 FPK%(4)=X%
620 FPK%(5)=Y%
640 FPK%(6)=7
660 FPK%(7)=2
680 FPK%(8)=0
700 DIM GA$(10),GB$(10),GC$(10),GD$(10)
720 DIM FR(200),E1(200),E2(200),E3(200),F(200),A(200),B(200),W(200)
740 DIM Y(200),X(200)
760 ONE% = 1% :TWO% = 2%:FLAG = 0
780 PRINT" ENTER:   FREP015.DAT (0); FREP.DAT (2); DEFAULT=FREP015.DAT    "
800 INPUT "          (3) TO ENTER OTHER FILENAME     ";Z%
820 IF (Z% = 3) THEN GOTO 840 ELSE GOTO 860
840 INPUT "          ENTER THE FILE NAME WITHOUT EXT.    "Y$:Y$=Y$+'.DAT'
860 IF Z% = 0 THEN Y$ = 'FREP015.DAT'
880 IF Z% = 2 THEN Y$ = 'FREP.DAT'
900 IF (Z% < 0) OR (Z% > 3 ) THEN GOTO 780
920 OPEN Y$ FOR INPUT AS FILE #3
940 PRINT:PRINT:CLS
960 INPUT "NO. OF PT TO BE GRAPHED (200 MAX); DEFAULT=50    ";I%
980 PRINT:PRINT
1000 IF (I% = 0) THEN I% = 50
1020 THOUS = 1000
1040 PRINT "          WISH THE POSITIVE  OF NEG. OF THE IMAG. COMPONENT  "
1060 INPUT "          P = POSITIVE, N = NEGATIVE (DEFAULT = N)    ";AN$W$
1080 IF (AN$W$ = "") THEN AN$W$ = 'N'
1100 IF (AN$W$ <> 'P') AND (AN$W$ <> 'N') THEN GOTO 1040
1120 FOR K% = ONE% TO I%
1140 ON ERROR GOTO 1280
1160         INPUT #3, FR(K%),E1(K%),E2(K%),E3(K%)
1180         !E1(K%) =  -E1(K%)
1200         IF (AN$W$ = 'N') THEN E2(K%) =  -E2(K%)
1220         F(K%)  =  E3(K%)
1240         E3(K%) =  LOG(E3(K%) * THOUS)  !CHANGE GHz TO MHz
1260 NEXT K%
1280 CLOSE #3:IF (ERL = 1140) THEN PRINT "ERROR READING FILE"
1300 BAT = Y% / E3(I%)                    !SETTING LARGEST VALUE TO WITHIN SCREEN
1310 REM  FINDING MAX VALUE OF REAL AND IMAG. COMPONENTS
1320 TEN = 10
1340 L1=E1(1): L2=E2(1): L3=E3(I%)/TEN
1360 FOR K% = ONE% TO I%
1380         E3(K%) = E3(K%) * BAT
1440         IF (E1(K%) > L1) THEN L1 = E1(K%)
1460         IF (E2(K%) > L2) THEN L2 = E2(K%)
1480 NEXT K%
1485 L4 = F(I%) * L2 / TEN
1500 REM       ASSIGNING VARIABLES FOR AXIS: GA$ = REAL; GB$ = IMAG.
1520 REM GC$ = Ln(FREQ): GD$ = FREQ. * IMAG.
1530 REM       NOTE: THIS PROCEDURE WORKS AS LONG AS THE VALUES ON THE
```

```
1531 REM AXIS ARE NOT EXPONENTIALS.  IN THIS CASE THE EXPONENT IS
1532 REM TRUNCATED FROM THE PRINTED VALUE ON THE AXIS.
1540 L = L1: L1 = L1/TEN: L2 = L2/TEN
1560 IT = INT(L1):E = L1 - IT: I$ = NUM$(IT): E$ = NUM$(E)
1580       E$ = MID(E$,2,5): GA$(1) = I$ + E$
1600 IT = INT(L2):E = L2 - IT: I$ = NUM$(IT): E$ = NUM$(E)
1620       E$ = MID(E$,2,5): GB$(1) = I$ + E$
1640 IT = INT(L3):E = L3 - IT: I$ = NUM$(IT): E$ = NUM$(E)
1660       E$ = MID(E$,2,5): GC$(1) = I$ + E$
1680 IT = INT(L4):E = L4 - IT: I$ = NUM$(IT): E$ = NUM$(E)
1700       E$ = MID(E$,2,5): GD$(1) = I$ + E$
1720 E1L = L1: E2L = L2: E3L = L3: FEL = L4 : TEN% = 10%
1740 FOR K% = TWO% TO TEN%
1760          E1L = E1L + L1
1780                IT = INT(E1L):E = E1L - IT:I$ = NUM$(IT)
1800                E$ = NUM$(E):E$ = MID(E$,2,5):GA$(K%) = I$ + E$
1820          E2L = E2L + L2
1840                IT = INT(E2L):E = E2L - IT:I$ = NUM$(IT)
1860                E$ = NUM$(E):E$ = MID(E$,2,5):GB$(K%) = I$ + E$
1880          E3L = E3L + L3
1900                IT = INT(E3L):E = E3L - IT:I$ = NUM$(IT)
1920                E$ = NUM$(E):E$ = MID(E$,2,5):GC$(K%) = I$ + E$
1940          FEL = FEL + L4
1960                IT = INT(FEL):E = FEL - IT:I$ = NUM$(IT)
1980                E$ = NUM$(E):E$ = MID(E$,2,5):GD$(K%) = I$ + E$
2000 NEXT K%
2010 REM      SCALING REAL AND IMAG. COMPONENTS TO SCREEN
2020 SCALE  = Y% / L
2040 FOR K% = ONE% TO I%
2060       E1(K%) = E1(K%) * SCALE
2080       E2(K%) = E2(K%) * SCALE
2100 NEXT K%
2120 CLS
2140 OPEN"$GR  " AS FILE #7
2160 CALL SYSFUNC(7,FPX%(1))
2180 PRINT "COLE-COLE PLOT (IMAG. VS. REAL): (1); REAL VS. Ln(freq.): (2)"
2200 PRINT "PRINT DATA: (3); QUIT: (4); REAL VS. (IMAG.* Ln(freq.)): (5)"
2220 INPUT "IMAG. VS. Ln(freq): (6)   ";IT%
2240 CLS
2260 IF (IT% = 1) THEN GOTO 2480
2280 IF (IT% = 2) THEN GOTO 3160
2300 IF (IT% = 3) THEN GOTO 4280
2320 IF (IT% = 4) THEN GOTO 4580
2340 IF (IT% = 5) THEN GOTO 4680
2360 IF (IT% = 6) THEN GOTO 8260
2380 IF (IT% < 1) OR (IT% > 6) THEN GOTO 2180
2420 CLS
2440 REM ***********************1111111111111111111111111***************************
2460 REM ***********************1111111111111111111111111***************************
2480 REM REAL VS IMAG.
2500 INPUT "X & Y AXIS SCALING FACTOR. DEFAULT = 1.55   ";SC$:SC = VAL(SC$)
2520 IF (SC = 0) THEN SC = 1.55
2540 IF (SC$ = "") THEN SC$ = NUM$(1.55)
2560 INPUT " WISH PTS. MARKED ON CURVE? Y = YES (DEFAULT = Y)    ";ANSW$
2580 IF (ANSW$ = "") THEN ANSW$ = 'Y'
2600 CLS
2620 SC$ = 'X & Y MULTIPLIED BY ' + SC$
2640 TEXT(95,400," IMAG. VS. REAL")
2660 TEXT(95,370,SC$)
2680 FOR K% = TWO% TO I%
2700       LINE(SC*E1(K%-ONE%),SC*E2(K%-ONE%)+50,SC*E1(K%),SC*E2(K%)+50)
2720          IF (ANSW$ = 'Y') THEN TEXT(SC*E1(K%-ONE%),SC*E2(K%-ONE%)+25+20,".")
2740 NEXT K%
2760 REM **********************    AXIS ROUTINE    **********************
2780 SCS = SC * SCALE:XINC = L1 * SCS: YINC = L2 * SCS
2800 X = 90
2820 Y = 760
2840 LINE(X,50,X,470)
2860 LINE(X,50,Y,50)
2880 FOR I = 1 TO 10 STEP 2
2900 TEXT(XINC*I,30,GA$(I))                    !X
2920 TEXT(0,I*YINC +50,GB$(I))                 !Y
2940 NEXT I
2960       A$CD$ = 'I'
2980 FOR J  = 1 TO 10
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```
3000 TEXT(XINC*J,40,A8CO$)
3020 TEXT(80,J*YINC + 50,"I",1,3)
3040 NEXT J
3060 FOR I = 1 TO 2.5E4:NEXT I
3080 GOTO 2180
3100 REM ********************2222222222222222222222**********************
3120 REM ********************2222222222222222222222**********************
3140 REM REAL VS. LOG(FREQ IN MHz)
3160 INPUT "X AXIS SCALING FACTOR. DEFAULT = 1.50    ";SC$:SC = VAL(SC$)
3180 IF (SC = 0) THEN SC = 1.50
3200 IF (SC$ = "") THEN SC$ = NUM$(1.50)
3220 INPUT " WISH PTS. MARKED ON CURVE? Y = YES (DEFAULT = Y)    ";AN$W$
3240 IF (AN$W$ = "") THEN AN$W$ = 'Y'
3260 IF I% )100 THEN FLAG = 1
3280 OPEN "GRAPHSUB.DAT" AS FILE #2
3300 PRINT "IS THE LAYOUT OF LAST SAMPLE CORRECT?   (Y = YES)    :"
3320 INPUT "          DEFAULT = Y      ";Y$
3340 IF (Y$ = "") THEN Y$ = 'Y'
3360 IF(Y$='Y')THEN INPUT#2,P$:INPUT#2,B$:INPUT#2,A$:INPUT#2,D$:GOTO 3540
3380 INPUT "NAME OF SAMPLE  :";P$ :P$ = P$ + ' VS AIR'
3400 INPUT"TIME WINDOW(nsec.)  :";B$ : B$ = B$ + ' NSEC. WINDOW'
3420 INPUT "EFFECTIVE DEPTH(mm)  P/W  :";A$,C$:A$='SSM = ' + A$+';'+C$+' PT'
3440 INPUT"DATE,FREQ RANGE IN GHz.  :"D$,E$:D$='DATE:'+D$+';'+E$+' GHz.'
3460 PRINT #2,P$
3480 PRINT #2,B$
3500 PRINT #2,A$
3520 PRINT #2,D$
3540 CLOSE #2
3560 CLS
3580 SC$ = 'X COORDINATE  MULTIPLIED BY ' + SC$
3600 TEXT(95,350," REAL VS. Ln(FREQ. IN MHz)")
3620 TEXT(95,320,SC$)
3640 FOR K% = TWO% TO I%
3660         LINE(SC*E3(K%-ONE%)+10,E1(K%-ONE%),SC*E3(K%)+10,E1(K%))
3680         IF (FLAG = 1) THEN GOTO 3720
3700         IF (AN$W$ = 'Y') THEN TEXT(SC*E3(K%-ONE%)+10,E1(K%-ONE%)-11,"*")
3720 NEXT K%
3740 IF (FLAG <> 1) THEN GOTO 3820
3760 FOR J% = TWO% TO I% STEP 10
3780         IF (AN$W$ = 'Y') THEN TEXT(SC*E3(J%-ONE%)+10,E1(J%-ONE%)-11,"*")
3800 NEXT J%
3820  TEXT(95,165,P$,2)
3840  TEXT (95,125,B$,2)
3860  TEXT (95,85,A$,2)
3880  TEXT (95,45,D$,2)
3900 REM **********************   AXIS ROUTINE   ********************
3920 XINC = L3 * SC * BAT: YINC = L1 * SCALE
3940 X = 90
3960 Y = 760
3980 LINE(X,50,X,470)
4000 LINE(X,50,Y,50)
4020 FOR I = 1 TO 9
4040 TEXT(XINC*I+10,30,GC$(I))              !X
4060 TEXT(0,I*YINC,GA$(I))                  !Y
4080 NEXT I
4100 !    A8CO$ = 'I'
4120 !FOR J  = 1 TO 10
4140 !TEXT(XINC*J,40,A8CO$)
4160 !TEXT(80,J*YINC + 50,"I",1,3)
4180 !NEXT J%
4200 FOR I = 1 TO 2.5E4 :NEXT I
4220 GOTO 2180
4240 REM ********************3333333333333333333333**********************
4260 REM ********************3333333333333333333333**********************
4280 INPUT" WISH A HARDCOPY OF PTS?  1 = Y  ";IT%
4300 IF (IT% <> 1) THEN GOTO 2180
4320 FPK%(10) = 6
4340 FPK%(11) = 2
4360 FPK%(12) = 3
4380 FPK%(13) = 2
4400 FPK%(14) = 0
4420 OPEN "$PR" FOR OUTPUT AS FILE #9
4440 PRINT #9, "FREQ. (MHz)      FREQ (RAD)       E1(K)          E2(K)"
4460 PRINT #9, "                 (per nsec.)"
4480 CALL SYSFUNC(9,FPK%(10))
```

```
4500 FOR K% = ONE% TO I%
4520       ON ERROR GOTO 4580
4540       PRINT #9, F(K%),FR(K%),E1(K%),E2(K%)
4560 NEXT K%
4580 CLOSE #9
4600 CLOSE #7
4620 STOP
4640 REM ********************555555555555555555555555**********************
4660 REM ********************555555555555555555555555**********************
4680 REM  E1(K) VS. (E2(K) * FREQ)
4700 PRINT "  WARNING, THE COMPUTER'S MEMORY MAY LOOSE DATA AFTER DOING"
4720 PRINT "THE LINEAR LEAST SQUARE ROUTINE; THUS, GRAPH THE DATA BEFORE"
4740 PRINT "DOING A SECOND LLS TO SEE IF THE DATA IS CORUPTED."
4760 INPUT "X AXIS SCALING FACTOR. DEFAULT = 2.50    ";SC$:SC = VAL(SC$)
4780 IF (SC = 0) THEN SC = 2.50
4800 IF (SC$ = "") THEN SC$ = NUM$(2.50)
4820 INPUT " WISH PTS. MARKED ON CURVE? Y = YES (DEFAULT = Y)    ";AN$W$
4840 IF (AN$W$ = "") THEN AN$W$ = 'Y'
4860 SC$ = 'X COORDINATE  MULTIPLIED BY ' + SC$
4880 PRINT " DESIRE FREQ. IN GHz. (0) OR radians/nsec. (1)    "
4900 INPUT "      DEFAULT = GHz.  (0)    ";SELECT
4920 IF (SELECT = 1) THEN GOTO 5160
4940 CLS
4960 TEXT(400,460," REAL VS. IMAG. * FREQ. IN GHz.")
4980 TEXT(400,445,SC$)
5000 FOR K% = TWO% TO I%
5020       A(K%) = E2(K%) * F(K%)
5040       B(K%) = E2(K%-ONE%) * F(K%-ONE%)
5060       LINE(SC*B(K%) + 90,E1(K%-ONE%),SC*A(K%) + 90,E1(K%))
5080       IF (AN$W$ = 'Y') THEN TEXT(SC*B(K%)+90,E1(K%-ONE%)-11,".")
5100 NEXT K%
5120 A(1) = B(2)
5140 GOTO 5320
5160 TEXT(400,450," REAL VS. IMAG. * FREQ. IN radians/nsec.")
5180 TEXT(400,420,SC$)
5200 FOR K% = TWO% TO I%
5220       A(K%) = E2(K%) * FR(K%)
5240       B(K%) = E2(K%-ONE%) * FR(K%-ONE%)
5260       LINE(SC*B(K%) + 90,E1(K%-ONE%),SC*A(K%) + 90,E1(K%))
5280       IF (AN$W$ = 'Y') THEN TEXT(SC*B(K%)+ 90,E1(K%-ONE%)-11,".")
5300 NEXT K%
5320 S2,D0,D1 = 0
5340 A(1) = B(2)
5360 REM **********************   AXIS ROUTINE   **********************
5380 XINC = L4 * SC * SCALE: YINC = L1 * SCALE
5400 X = 90
5420 Y = 760
5440 LINE(X,50,X,470)
5460 LINE(X,50,Y,50)
5480 FOR I = 1 TO 10 STEP 2
5500 TEXT(XINC*I+90,30,CO$(I))              !X
5520 TEXT(0,I*YINC,GA$(I))                  !Y
5540 NEXT I
5560 !     ABCD$ = 'I'
5580 !FOR J  = 1 TO 10
5600 !TEXT(XINC*J,40,ABCD$)
5620 !TEXT(80,J*YINC + 50,"I",1,9)
5640 !NEXT J%
5660 FOR I = 1 TO 2.5E4:NEXT I
5680 INPUT" WISH LINEAR LEAST SQ. DONE?  (Y=YES):    ";Y$
5700 IF (Y$ <> 'Y') THEN GOTO 2180
5720 CLS
5740 REM LLS ROUTINE
5760 REM PROGRAM FROM Wilkins,Klopfenstein,Isenhour and Jurs, INTRODUCTION
5780 REM TO COMPUTER PROGRAMMING FOR CHEMISTS  BASIC VERSION (1974) p.301
5800 REM
5820 REM N% = # PTS. USED IN LLS; I% = TOTAL # PTS.
5840 REM E1() AND E2() WERE SCALED TO FIT THE SCREEN BY SCALING FACTOR "SCALE"
5860 REM THEY ARE DIVIDED BY "SCALE" BEFORE THE LLS IS DONE.
5880 REM E1() = REAL COMPONENT; A() = IMAG. * FREQ. (IN GHz. or rad/nsec.)
5900 REM
5920 INPUT" NO. PTS. FROM END THAT WILL NOT BE USED   :";NP%
5940 INPUT" NO. PTS. FROM BEGINNING NOT USED  (DEFAULT = 0)    ";NB%
5960 IF (NB% = 0) THEN NB% = 0
5980 PRINT "WEGHTING OF DATA: UNIT(1) OR INVERSE(2)  :"
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6000 INPUT "DEFAULT = UNIT   ";N9%
6020 IF (N9% = 0) THEN N9% = 1
6040 IF (N9% <> 1) AND (N9% <>2) GOTO 5980
6060 REM Initialize the data for LLS and the GRAPH
6080 N% = I% - NP% : MIL = 1E6
6100 FOR J% = ONE% TO N%
6120       Y(J%) = E1(J%)
6140       X(J%) = A(J%)
6160       E1(J%) = E1(J%) / SCALE * MIL  ! Y COORDINATE    Y(I)
6180       A(J%)  = A(J%) / SCALE  * MIL  ! X COORDINATE    X(I)
6200       IF (N9% = 1) THEN W(J%) = 1 ELSE W(J%) = 1 / E1(J%)
6220 NEXT J%
6240 GOTO 6460
6260 REM
6280 REM
6300 INPUT" NO. PTS. FROM END THAT WILL NOT BE USED   :";NP%
6320 INPUT" NO. PTS. FROM BEGINNING NOT USED  (DEFAULT = 0)    ";N8%
6340 IF (N8% = 0) THEN N8% = 0
6360 PRINT "WEGHTING OF DATA: UNIT(1) OR INVERSE(2)  :"
6380 INPUT "DEFAULT = UNIT   ";N9%
6400 IF (N9% = 0) THEN N9% = 1
6420 IF (N9% <> 1) AND (N9% <>2) GOTO 6360
6440 N% = I% - NP%
6460 PRINT " FREQ. IN GHz. OF 1ST. PT.  :";F(N8%)
6480 PRINT " FREQ. IN GHz. OF LAST PT.  :";F(N%)
6500 INPUT " WISH A GRAPH OF THIS FREQ. RANGE? Y = YES   ";GR$
6520 CLS
6540 IF (GR$ <> 'Y') THEN GOTO 6640
6560 FOR K% = N8% TO N%
6580       LINE(SC%*8(K%) + 14,Y(K%-ONE%),SC%X(K%) + 14,Y(K%))
6600       IF (ANS$ = 'Y') THEN TEXT(SC%8(K%)+ 14,Y(K%-ONE%)-11,".")
6620 NEXT K%
6640 INPUT " WISH TO CHOOSE ANOTHER PT?  (Y = YES)    :";Y$
6660 CLS
6680 IF (Y$ = 'Y') THEN GOTO 6300
6700 IF (N9% = 1) THEN GOTO 6780
6720 FOR J% = ONE% TO N%
6740       W(J%) = 1 / E1(J%)
6760 NEXT J%
6780 GOSUB  7780                          ! SUMMATION ROUTINE
6800 GOSUB  7000                          ! PRINT ROUTINE
6820 INPUT " WISH ANOTHER LINEAR LEAST SQ.  (Y = YES):    ";Y$
6840 IF (Y$ ='Y') THEN GOTO 6300
6850 MIL = 1E6
6860 FOR J% = ONE% TO N%
6880       E1(J%) = E1(J%) * SCALE  / MIL
6900       A(J%)  = A(J%)  * SCALE  / MIL
6920 NEXT J%
6940 GOTO 2180
6960 REM
6980 REM ****************    PRINT ROUTINE  ************************
7000 PRINT:PRINT
7020 M% = N% - N8%
7040 XXX = 1/A1
7045 PRINT "THE ORIGINAL NO. ARE MULT. BY 1E6. THE INTERCEPT IS * 1E6"
7060 PRINT "INTERCEPT",A0,"STD DEV",D0
7080 PRINT "    "
7100 PRINT "SLOPE",A1,"STD DEV",D1
7120 PRINT "    "
7140 PRINT "1/SLOPE",XXX
7160 PRINT "    "
7180 PRINT "OVERALL STD DEV    "D"  BASED ON"M%"DATA POINTS"
7200 PRINT:PRINT
7220 INPUT" DO YOU WISH A TABLE (Y = YES)    :";Y$
7240 IF (Y$ <> 'Y') THEN GOTO 7720
7260 INPUT" WANT A HARD COPY? (Y = YES)  :";Y$
7280 IF (Y$ <> 'Y') THEN GOTO 7400
7300 DATA 6,2,3,2,0: READ FPK%(J%+14) FOR J% = ONE% TO 5%: FL = 3
7320 OPEN "$PR" FOR OUTPUT AS FILE #9
7340 CALL SYSFUNC(9,FPK%(15))
7360 PRINT #9,"INTERCEPT",A0,"STD DEV",D0
7380 PRINT#9,"    "
7400 PRINT #9,"SLOPE",A1,"STD DEV",D1
7420 PRINT#9,"    "
7440 PRINT #9,"1/SLOPE",XXX
```

```
7460 PRINT #9,"OVERALL STD DEV   "D"  BASED ON"M%"DATA POINTS"
7480 PRINT #9:PRINT#9
7500 PRINT #9,"POINT #"," X VALUE","Y VALUE","WEIGHT"," CALC. Y VALUE"
7520 FOR J% = N8% TO N%
7540       PRINT#9,I,A(J%),E1(J%),W(J%),A0+A1*A(J%)
7560 NEXT J%
7580 CLOSE #9
7600 PRINT:PRINT
7620 PRINT"POINT #"," X VALUE","Y VALUE","WEIGHT"," CALC. Y VALUE"
7640 PRINT:PRINT
7660 FOR J% = N8% TO N%
7680       PRINT J%,A(J%),E1(J%),W(J%),A0+A1*A(J%)
7700 NEXT J%
7720 RETURN
7740 REM
7760 REM ****************  SUMMATION ROUTINE  ***********************
7780 Z0,Z1,Z2,Z3,Z4,Z5 =0
7800 A0,A1,Q,D = 0
7820 FOR J% = N8% TO N%
7840       Z0 = Z0 + W(J%)
7860       Z1 = Z1 + W(J%) * A(J%)
7880       Z2 = Z2 + W(J%) * E1(J%)
7900       Z3 = Z3 + W(J%) * A(J%) * E1(J%)
7920       Z4 = Z4 + W(J%) * A(J%) * A(J%)
7940       Z5 = Z5 + W(J%) * E1(J%) * E1(J%)
7960 NEXT J%
7980 D  = Z0 * Z4 - Z1 * Z1
8000 A0 = (Z4 * Z2 - Z1 * Z3) / D
8020 A1 = (Z0 * Z3 - Z1 * Z2) / D
8040 Q  = 0
8060 FOR J% = N8% TO N%
8080       Q = Q + W(J%) * (E1(J%) - A0 - A1 * A(J%)) ^ 2
8100 NEXT J%
8120 S2 = Q / (N% -2)                        ! NOTE N% - 2 METHOD
8140 D0 = SQR(S2 * Z4 / D)
8160 D1 = SQR(S2 * Z0 / D)
8180 D  = SQR(S2)
8200 RETURN
8220 REM ***************************6666666666666666666666***********************
8240 REM ***************************6666666666666666666666***********************
8260 REM IMAG. VS. LOG (FREQ. IN MHz.)
8280 INPUT "X & Y AXIS SCALING FACTOR. DEFAULT = 1.50   ";SC$:SC = VAL(SC$)
8300 IF (SC = 0) THEN SC = 1.50
8320 IF (SC$ = "") THEN SC$ = NUM$(1.50)
8322 INPUT "Y AXIS TO BE SCALE SAME AS X ? DEFAULT = YES  ";YAXI$
8323 IF (YAXI$ = "") THEN SC1 = SC : YAXI$ = "Y" : GOTO 8340
8325 INPUT "Y AXIS SCALING FACTOR  ";SC1  : SC1$ = NUM$(SC1)
8340 INPUT " WISH PTS  MARKED ON CURVE? Y = YES (DEFAULT = Y)    ";AN5W$
8350 PRINT$ = "X & Y COORDINATE NO. ARE MULTIPLIED BY "
8360 IF (AN5W$ = "") THEN AN5W$ = 'Y'
8362 IF (YAXI$ <>'Y') THEN SC$ = PRINT$ + SC$ + 'AND '+ SC1$: GOTO 8400
8380 SC$ = PRINT$ + SC$
8400 IF I% >100 THEN FLAG = 1
8420 OPEN "GRAPHSU1.DAT" AS FILE #2
8440 PRINT "IS THE LAYOUT OF LAST SAMPLE CORRECT?   (Y = YES)    :"
8460 INPUT "          DEFAULT = Y    ";Y$
8480 IF (Y$ = "") THEN Y$ = 'Y'
8500 IF(Y$='Y')THEN INPUT#2,P$:INPUT#2,B$:INPUT#2,A$:INPUT#2,D$:GOTO 8680
8520 INPUT "NAME OF SAMPLE  :";P$ :P$ = P$ + ' VS AIR'
8540 INPUT"TIME WINDOW(nsec.)  :";B$ : B$ = B$ + ' NSEC. WINDOW'
8560 INPUT "EFFECTIVE DEPTH(mm), P/W  :";A$,C$:A$='SSM =.' + A$+';'+C$+' PT'
8580 INPUT"DATE,FREQ RANGE IN GHz.  :"D$,E$:D$='DATE:'+D$+';'+E$+' GHz.'
8600 PRINT #2,P$
8620 PRINT #2,B$
8640 PRINT #2,A$
8660 PRINT #2,D$
8680 CLOSE #2
8690 INPUT " INPUT Y AXIS OFFSET, DEFAULT = 50    ";OFFY$
8692 IF (OFFY$ = "") THEN O% = 50 ELSE O% = VAL(OFFY$)
8700 CLS
8720 TEXT(95,250,"IMAG. VS. LOG (FREQ. IN MHz.)")
8740 TEXT(95,210, SC$)
8760 FOR K% = TW0% TO I%
8780       LINE(SC*E3(K%-ONE%)+10,SC1*E2(K%-ONE%)+O%,SC*E3(K%)+10,SC1*E2(K%)+O%)
```

```
8800        IF (FLAG = 1) THEN GOTO 8840
8820        IF (AN5W$='Y') THEN TEXT(SC*E3(K%-ONE%)+10,SC1*E2(K%-ONE%)-11+0%,"*")
8840 NEXT K%
8860 IF (FLAG <> 1) THEN GOTO 8940
8880 FOR J% = TW0% TO I% STEP 10
8900        IF (AN5W$='Y') THEN TEXT(SC*E3(J%-ONE%)+10,SC1*E2(J%-ONE%)-11+0%,"*")
8920 NEXT J%
8940 TEXT(95,400,P$,3)
8960 TEXT (95,370,B$,2)
8980 TEXT (95,330,A$,2)
9000 TEXT (95,290,D$,2)
9020 REM ********************   AXIS ROUTINE   **********************
9040 XINC = L3 * SC * BAT: YINC = L2 * SC1 * SCALE
9060 X = 90
9080 Y = 760
9085 00% = 0% - 29
9100 LINE(X,50,X,470)
9120 LINE(X,50,Y,50)
9140 FOR I = 1 TO 10 STEP 2
9160 TEXT(XINC*I+10,30,GC$(I))              !X
9180 !     TEXT(0,I*YINC+21,GB$(I))           !Y
9182 TEXT(0,I*YINC+00%,GB$(I))              !Y
9200 NEXT I
9220 !          A8CD$ = 'I'
9240 !FOR J = 1 TO 10
9260 !TEXT(XINC*J,40,A8CD$)
9280 !TEXT(80,J*YINC + 50,"I",1,3)
9300 !NEXT J%
9320 FOR I = 1 TO 2.5E4 :NEXT I
9340 GOTO 2180
9360 END
```

APPENDIX F
COMPUTER PROGRAM USED TO INTERFACE THE IBM CS-9000 COMPUTER WITH THE VAX 11/780 COMPUTER

TALK9.BAS..... 260

The program titled TALK9.BAS is used to interface the IBM CS-9000 computer with the VAX 11/780 computer.

```
4 CLS
5 TEXT (200,400,"IF ALL POSSIBLE")
6 TEXT (200,300,"NEVER ",3)
7 TEXT (200,200,"USE (CTRL)(ALT)(DEL)",2)
8 TEXT (200,100,"TO BREAK FROM PROGRAM")
9 !FOR I=1 TO 500:X=SIN(I):NEXT I:CLS
10 PRINT "   THIS PROGRAM WILL COMMUNICATE WITH ANOTHER SYSTEM.  IT WILL PROMPT"
11 PRINT "FOR THE SYSTEM PARAMETERS.  IT PROVIDES A METHOD FOR FILE TRANSFERS."
12 PRINT "PROGRAMS CONNECTS THROUGH SERIAL PORT #2"
15 PRINT
16 PRINT "          TO USE PROGRAM: "
18 PRINT "          ENTER (CTRL) A WHEN PROMPTED, 3, (CR) "
19 PRINT "          NOW LOGIN TO OTP VAX: "
21 PRINT "          EITHER (1): TYPE D, (CR), (CR), "
22 PRINT "          ENTER PHONE # (2-5469 OR 2-5290), (CR), (CR) "
24 PRINT "          OR (2) TYPE R1, (CR), (CR) "
29 INPUT "  TO CONTINUE WITH THE PROGRAM ENTER A (CR)",AB$
30 ON ERROR GOTO 650
40 DIM FPK%(23)
51 BRATE=1200 : SBIT=1 : DBIT=8 : P$='NONE' : PORT$= '@SER02'
52 ECHO$='N' : CRLF$ = 'N'
60 FPK%(1) = 20                                  !SET BAUD RATE TO 1200
61 FPK%(2) = 8
140 FPK%(3) = 22                                 !SET STOP, DATA, & PARITY
160 S1 = -1                                      !SET ILLEGAL ENTRY FLAG
170 IF SBIT = 1 THEN S1 = 64
220 D1 = (DBIT -5)*4                             !SET THE PROPER BIT NUMBER = 12
250 P1 = 0                                       !SET PARITY TO NONE
280 FPK%(4)=S1+P1+D1
290 FPK%(5) = 6                          !RECEIVE TIMEOUT FUNCTION
300 FPK%(6) = 60                         !SET TIMEOUT TO 3 SEC
310 FPK%(7) = 2                          !SET MODE BITS
312 FPK%(8) = $1848
313 FPK%(9) = $1808
320 FPK%(18) = 4                         !TRANSMIT TIMEOUT FUNCTION
321 FPK%(19) = 80                        !SET TIMEOUT TO 4 SEC
330 FPK%(10) = 0                         !END FUNCTION FPK%(1)
340 FPK%(12) = 38                        !SEND BREAK FUNCTION FOR 100 MS
350 FPK%(13) = 2
360 FPK%(14) = 0                         !END FUNCTION FPK%(12)
361 FPK%(15) = 39                        !RESET PORT
362 FPK%(16) = $1808                     !END PACKAGE FPK%(15)
365 CALL SYSOPEN (2.0,PORT$,2.0,0,1,PORPTR)
390 CLS
400 LF%=2560
410 TEXT(200,300," THIS IS A TERMINAL EMULATION PROGRAM ")
420 CALL SYSFUNC (2,FPK%(1))                     !SET UP PORT
425 OPEN PORT$ AS FILE #5
430 CALL SYSOPEN(7.0,'@CON  ',1.0,0,1,CONPTR)
440 CALL SYSOPEN (6,'@SCRN0',2.0,0,1,SCRPTR)
480 REM
485 TEXT(200,350, "ENTER   (CTRL) A   TO TRANSFER FILES OR EMULATE  ")
486 REM ************************************************************
487 REM
490 CALL BREAD(CONPTR,5%)
510 IF 5% = 7681 THEN 729                        !CTRL A
520 IF 5% () 12290 THEN 560
530 CALL SYSFUNC (2,FPK%(12))                    !SEND BREAK
540 GOTO 490
545 PRINT
550 PRINT "  WRITING OUT THE CHARACTER TO THE SERIAL PORT"
555 PRINT
560 CALL BWRITE(PORPTR,5%)
570 REM  IF CARRIAGE RETURN THEN SEND LINE FEED IF SELECTED
580 IF (5% = 7181) AND (CRLF$ = 'Y') THEN CALL BWRITE(PORPTR,LF%)
590 REM  TESTING THE SERIAL INPUT TO SEE IF CHARACTER RECEIVED
600 CALL BREAD(PORPTR,V%)
610 IF V% () -7670 THEN CALL BWRITE(SCRPTR,V%)
620  IF ECHO$ = 'Y' THEN CALL BWRITE(PORPTR,V%)
630 GOTO 490
635 REM ************************************************************
```

```
636 REM
640 REM ON ERROR STATEMENT BRANCHES HERE WHEN NO DATA AVAILABLE
650 IF ERL = 490 THEN RESUME 600
660 IF ERL = 600 THEN RESUME 490
670 IF ERL = 560 THEN RESUME 600
680 IF ERL = 1010 THEN RESUME 900
685 !IF ERL = 820 THEN RESUME 820
690 IF ERL = 870 THEN RESUME 895
700 IF ERL = 970 THEN RESUME 970
705 IF ERL <> 880 THEN GOTO 710
706 CALL SYSFUNC(2,FPK%(15))                    !RESET PORT
707 RESUME 885                                  !RETURN TO SENDING FILE TO PORT
710 PRINT "ERROR OCCURRED";ERL
720 GOTO 1050
729 CLS
730 INPUT "FILE TRANSFER ROUTINE ENTER 1-SEND,2-RCV,3-EMUL,4-STOP ";M
750 CLS
755 IF (M ) 4) OR (M ( 1) THEN GOTO 730
760 ON M GOTO 770,930,490,1050
761 REM ************************************************************
762 REM
765 REM       THE LINE SENT IS COMPARED WITH THE RECEIVED LINE.  IF THEY
766 REM  DON'T MATCH, THE LINE IS WRITTEN TO THE SCREEN & REWRITTEN
767 REM  TO THE PORT
770 PRINT "  SENDING FILE TO SERIAL PORT"
780 REM KEEP READING UNTIL REACH EOF
790 INPUT "IBM CS9000 FILE NAME ";F$
800 OPEN F$ FOR INPUT AS FILE #6
801 PRINT #5, "SET TERM/HOSTSYN/WIDTH= 511" : INPUT LINE #5,N$
802 INPUT LINE #5,N$
803 INPUT "VAX FILENAME WITH EXTENSION AND VERSION # ";F$
805 PRINT #5, "COPY TT: ",F$
807 INPUT LINE #5,M$
855 PRINT " READING LINE OF FILE"
856 REM L% = LINE # BEING SENT
860 L% = 0
870 INPUT LINE #6,M$
880 PRINT #5,M$;                                !SEND LINE OF FILE
881 L% = L% + 1
885 INPUT LINE #5,N$
887 L$ = RIGHT(N$,2)
889 IF L$ = M$ THEN GOTO 870
890 PRINT L%;M$;
891 PRINT L%;L$;
892 GOTO 885
895 V% = $1A!A
897 CALL BWRITE(PORPTR,V%)
900 CLOSE #6
910 TEXT (100,200,"TRANSFER COMPLETE",2)
920 GOTO 490                                    !RESUME EMULATION
921 REM ************************************************************
922 REM
930 PRINT " READ A FILE FROM SERIAL PORT AND STORE"
940 INPUT " IBM CS9000 FILE NAME ";F$
942 !KILL F$
945 !INPUT YOU WISH TO CONTINUE  1 = Y  ";ANSW
946 ! IF(ANSW () 1) THEN GOTO 485
950 OPEN F$ FOR OUTPUT AS FILE #6
953 INPUT "VAX FILENAME WITH EXTENSION AND VERSION # ";F$
955 PRINT #5,"@SYS$MANAGER:GET.COM "+F$
957 INPUT LINE #5,M$
1010 INPUT LINE #5,M$                           !INPUT LINE FROM PORT
1020 A$ = CVT$$(M$,4%)
1027 IF MID(M$,2,4) = "%EOF" THEN GOTO 900
1030 PRINT #6,A$                                !SENDING LINE TO DISK
1040 GOTO 1010                                  !LOOP TILL TIMEOUT OF EOF
1041 REM ************************************************************
1042 REM
1050 CLOSE #5
1060 CLOSE #6
1070 CLOSE #7
1080 CLOSE #2
1090 REM VALID BAUD RATES
1100 DATA 45.5,75,110,134.5,150,300,600,1200,1800,2000,2400,4800&
        ,9600,19200,38400
```

```
1110 END
```

APPENDIX G
COMPUTER PROGRAM USED TO SIMULATE THE TIME DOMAIN DATA

INVD3.FOR..... 265

The program titled INVD3.FOR simulates the time domain data by manipulating the reference waveform. The original program was written by Doan.

```
$ ASSIGN TT FOR005
$ ASSIGN TT FOR006
$ ASSIGN CTIME.TXT FOR007
$ ASSIGN OUT.TXT FOR004
$ IF P1 .EQS. "" THEN INQUIRE P1 "ENTER REFERENCE, NO EXT."
$ ASSIGN 'P1'.DAT FOR011
$ ASSIGN INVERSE.DAT FOR003
$ ON CONTROL_Y THEN $ GOTO DONE
$ RUN RSD$DISK:[ES]INVD3B.EXE
$ DONE:
$ DEASSIGN FOR003
$ DEASSIGN FOR004
$ DEASSIGN FOR005
$ DEASSIGN FOR006
$ DEASSIGN FOR007
$ DEASSIGN FOR011
```

```
      PROGRAM INVD3B
C     Simulates a time domain spectrum data
      IMPLICIT COMPLEX (A-C)
      COMPLEX QZERO
      REAL *4 A1,B1,BSR
      INTEGER FLAG
      DIMENSION W(2048),ARF(2048)
      DIMENSION REF(2048),CFR(2048),EPS(5),TAU(5)
      DIMENSION UNREAL(2048),RACCUM(2048),TM(2048)
      DIMENSION CTIME(1024),ACCTM(1024),CSIMUL(2048)
C
C              %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
C              %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
C
      WRITE (5,*) ' COPYING REF. DATA FROM DISK'
      READ (11,*) NPO
      READ (11,*) VCRD
      READ (11,*) HCRD
      VCRD = VCRD / 1000.
      DO 10 K = 1, NPO
            READ (11,*) REF(K)
            REF(K) = REF(K) * VCRD
 10   CONTINUE
      READ (3,*) SG
      READ (3,*) RS
      READ (3,*) RR
      READ (3,*) TTOT
      READ (3,*) NDL
      READ (3,*) NBA
      READ (3,*) FRMX
      READ (3,*) FRMN
      READ (3,*) NFR
      READ (3,*) SD
      READ (3,*) IP
      READ (3,*) NPO
      WRITE (5,*) ' CONDUCTIVITY FROM DSAM7.FOR       ',SG
      WRITE (5,*) ' AVG. OF FINAL VALUES OF DIF ARRAY',RS
      WRITE (5,*) ' AVG.                        SUM   ',RR
      WRITE (5,*) ' TOTAL TIME OF TRACE ON SCOPE      ',TTOT
      WRITE (5,*) ' # OF DELAY ADDRESSES              ',NDL
      WRITE (5,*) ' # OF BASELINE AVG.                ',NBA
      WRITE (5,*) ' MAX FREQ. IN RADIANS PER nsec.    ',FRMX
      WRITE (5,*) ' MIN                               ',FRMN
      WRITE (5,*) ' # OF FREQ. PT IN DSAM7.FOR        ',NFR
      WRITE (5,*) ' EFFECTIVE SAMPLE DEPTH            ',SD
      WRITE (5,*) ' TIMING MARKER ADDRESS             ',IP
      WRITE (5,*) ' # PT. IN REFD011 DAT              ',NPO
      WRITE (5,*) '     '
      WRITE (5,*)'          ZEROING ALL DATA.    '
      WRITE (5,*)'        '
      DATA ZERO,ONE,TWO/0.,1.,2./
      DATA THIRTY,QUART,TPI/30.,.25,6.2831853/
      QZERO = CMPLX(ZERO,ZERO)
      DO 3 K = 1,NPO
          W(K) = ZERO
          ARF(K)  = QZERO
          CFR(K)  = QZERO
          UNREAL(K)  = ZERO
          RACCUM(K)  = ZERO
 3     CONTINUE
       DO 2, K = 1,5
          EPS(K)  = ZERO
 2        TAU(K)  = ZERO
C
C            MAX. VALUE OF w. ( (=3.14/TI)'
C
C
C
C
      WRITE (5,*) '  NO. OF SMOOTHING ITERATIONS  '
      READ(6,*)  ISM
C
      WRITE(5,*) 'THE TOTAL TIME WANTED FOR THE
     * SPECTRUM--DEFAULT - 0 - USES'
```

```
        WRITE (5,*) '     THE EXPERIMENTAL SPECTRUM TIME. '
        WRITE (5,*) ' NO. OF RELAXATION TIMES (5 MAX) '
        READ(6,*)  TIME,NRLX
C
       WRITE (5,*) ' WISH TO DO AN INVERSE LAPLACE ON THE
     * REFERENCE; ENTER 1'
       WRITE (5,*) '      SAMPLE;  ENTER ZERO(0), ENTER (3)
     * FOR DIFFERENCE'
       READ(6,*) FLAG
        IF (FLAG .EQ. 1) GOTO 11
C
       WRITE (5,*) ' HIGH FREQ. DIELECTRIC CONSTANT , '
        WRITE (5,*) ' THE CORR. FACTOR (2Vo/(Vo+Vr)) IF
     * THE SAMPLE IS CONDUCTING;'
       WRITE (5,*) '      USE 1. IF NONCONDUCTING. (NOT FUNCTIONAL AS YET)'
       READ(6,*)  EINF,SIGMA
C
        WRITE (5,*) ' THE DIELECTRIC LOSS DURING THE Kth
     ' RELAXATION ie. THE Eo - E(inf) '
       WRITE (5,*) '      of the  Kth relaxation;
     *      AND TAU VALUE FOR THE Kth. '
       WRITE (5,*) '   RELAXATION.'
C
C
       DO 18 K=1,NRLX
  18        READ(6,*)   EPS(K),TAU(K)
C
C
C
C
 11     CONTINUE
       WRITE (5,*) ' ENTER NO. OF TIME PTS. IN INVERSE FT. '
       READ(6,*) NTM
       WRITE (5,*) ' ENTER NO. OF FREQ. DOMAIN PTS. IN FT. '
       READ(6,*) NFR
C
C
C                      BASELINE AND BASELINE CORRECTIONS
C**********************************************************************
C**********************************************************************
        WRITE (5,*)' ENTER NO. OF PT. TO SKIP FROM BEGINNING OF
     *TIMEWINDOW '
        READ(6,*) IP
        BSR = ZERO
        IONE = 1
        NOP = IP + NBA
C       SMOOTH BASELINE 40 TIMES TO REMOVE DISTORTIONS DUE TO THE
C       TIMING MARKER AND THE RANDOM VALUE OF THE INITIAL POINTS.
C       THESE DISTORTIONS WILL CAUSE FALSE HIGH FREQ. DATA.
C
        JST = IP + 1
        ILOOP = 40
        CALL SMOOTH(NBA,REF,ILOOP,JST)
        DO 57 INDEX = 1,2
C          FIND AVERAGE BASELINE VALUE AFTER THE IPth. POINT
C
           DO 50 K = 1 , NBA
 50              BSR=BSR + REF(K + IP)
           BSR = BSR / (REAL(NBA))
C          SET THE 1st. IP POINTS TO THE AVERAGE VALUE - BSR
           DO  55 K = 1,IP
 55              REF(K) = BSR
C          SMOOTH BASELINE 6 TIMES TO REMOVE DISTORTIONS
C
           IF (INDEX .EQ. 1) THEN
              BSR = ZERO
              CALL SMOOTH(NOP,REF,ILOOP,IONE)
           ELSE
           END IF
 57     CONTINUE
        DO 58 K = 1,NP0
           REF(K) = REF(K) - BSR
 58     CONTINUE
C**********************************************************************
C**********************************************************************
```

```
C                   SMOOTHING ALL REFERENCE DATA
C
      WRITE (5,*) ' SMOOTHING ALGORITHM IN PROCESS'
      CALL SMOOTH(NP0,REF,ISM,IONE)
C
      WRITE (5,*) ' DESIRE TO USE ONLY 1/2 PTS   (1 = YES)'
      READ(6,*) IANSW
      IF (IANSW .EQ. 1) THEN
           NP0 = NP0 / 2
           DO 30 K = 0,NP0
 30              REF(K+1) = REF(2 * K + 1)
      ELSE
      END IF
      TI = TTOT / REAL(NP0-1)
      WRITE (5,*) ' WISH TO REMOVE PART OF BASELINE PTS?
     * (1 = YES)'
      READ (6,*) IANSW
      IF (IANSW .EQ. 1) THEN
           WRITE (5,*) ' INPUT NO. OF PTS. TO REMOVE'
           READ (6,*) I
           NP0I = NP0 - I
           DO 60 K = 1,NP0I
                 REF(K) = REF(K + I)
 60         CONTINUE
            NP = NP0I
            NP0 = NP0I
      ELSE
       END IF
      NP = NP0
      IF (TIME.NE.0.) GOTO 70
      TIME = TI * REAL(NP - 1)
 70   CONTINUE
C
C
C
      WRITE (5,*)' DESIRE WINDOWING OF SAMPLE? 1 = YES.'
      READ(6,*) IWIND
      IF (IWIND .EQ. 1) THEN
          WRITE (5,*)'        '
          WRITE (5,*)' ENTER NO. OF DIVISION THE REF. CURVE
     * WILL BE DIVIDED'
          WRITE (5,*)' INTO FOR THE EXTENDED COSINE BELL WINDOWING'
          READ(6,*) NDV
          WRITE (5,*)'        '
          WRITE (5,*)' DESIRE ONLY END OF DATA WINDOWED?  1 = YES   '
          READ(6,*) IWIND
          NN = NP / NDV
          NNN = (NDV-1) * NN
          HALF = .5
          ONE  = 1.
          FIVE = 5.
          RNP = REAL(NP)
          TPIFIV = TPI * FIVE/RNP
          DO 39 K = 1,NP
               IF (K .LT. NN) THEN
                         IF (IWIND .EQ. 1) GOTO 39
                         FNCK = TPIFIV * REAL(K)
                         DD = HALF*(ONE-COS(FNCK))
                         REF(K) = REF(K) * DD
                    ELSE IF (K .GT. NNN) THEN
                         FNCK = TPIFIV * REAL(K)
                         DD = HALF*(ONE-COS(FNCK))
                         REF(K) = REF(K) * DD
                    ELSE
               END IF
 39       CONTINUE
      ELSE
      END IF
C
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
        WRITE (5,*)'     TRANSFORMING REFERENCE TO (iw)V(iw)'
C
C
```

```
      WRITE (5,*)'          '
      WRITE (5,*)'          '
 80   WRITE (*,*) ' DO YOU WISH A PRINT OUT OF Hz TO radians, 1=YES'
      READ(6,*) M
      IF (M .EQ. 1) CALL PFREQ
      WRITE (5,*)' ENTER FRMX  '
      READ(6,*) FRMX
      WRITE (5,*)'  FRMN  '
      READ(6,*) FRMN
      DFR = (FRMX - FRMN) / REAL(NFR -1)
      WRITE (5,*) '    '
      WRITE (5,*)' FREQ. INCREMENT (DFR)   ',DFR
      WRITE (5,*)'     '
      WRITE (5,*) ' WISH TO INPUT OTHER FREQ. RANGES? (1 = YES) '
      READ(6,*) IANSW
      IF (IANSW .EQ. 1) GOTO 80
      OM = FRMN
       WRITE (5,*) ' TRANSFORMING TIME DOMAIN DATA TO FREQ.'
C
C        FORWARD DFT EQ. :
C                                  N -1
C     X(k * df) = dt * SUM  [x(n * dt) * exp(-i2(PI)(k * df)(n * dt))]
C                                  n = 0
C
C        INVERSE DFT EQ. :
C                                  N -1
C     X(n * dt) = df * SUM  [X(n * df) * exp(i2(PI)(k * df)(n * dt))]
C                                  k = 0
C
C
C       where:
C                i = SQRT(-1)
C                (k * df) = freq. of kth. pt.
C                (n * dt) = time  of nth. pt.
C                x = time  domain pts.
C                X = freq. domain pts.
C
C
C      TM(J) = TIME OF EACH PT. IN DFT, USING TTOT AS THE TIME OF THE
C      SPECTRUM
C
C             J = TIME  LOOP
C             K = FREQ. LOOP
C
      DO 100 J = 1,NPO
 100        TM(J) = TI * REAL(J)
       TITWO = TI / TWO
       NPD1 = NPO - 1
       ATI = CMPLX(TI,ZERO)
       DO 150 K = 1,NFR
           A1    = ZERO
           B1    = ZERO
           W(K)  = OM
           DO 160 J = 1,NPD1
                T   = TM(J) * OM
                 D1 = REF(J)
                A1 = A1 + D1 * COS(T)
                B1 = B1 - D1 * SIN(T)
 160       CONTINUE
           ARF(K) = CMPLX(A1,B1) *  ATI
           OM = OM + DFR
 150   CONTINUE
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
       IF (FLAG .NE. 1) THEN
           CALL BEE(EINF,EPS,W,NFR,NRLX,ARF,SD,REF,TAU,CFR)
       ELSE
           WRITE (5,*) ' ONLY DOING FT ON REF    '
       END IF
       WRITE (5,*)' TRANSFORMING FREQ. DATA BACK TO THE TIME DOMAIN'
C      TITWO = TI / TWO
       I2FLAG = 3
       IF (I2FLAG .EQ.5)  THEN
C
C
        CT = CMPLX(0.,0.)
```

```
       T11=TIME/(NTM-1)
              WRITE (5,*)' T11  ',T11
       DO 2000 J=1,NTM
       AC=CMPLX(0.,0.)
       PH1=DFR*J*T11/2
       DO 5000 K=1,NFR-1
       CG=CMPLX(0.,(W(K)+DFR/2.)*T11*J)
 5000  AC=AC+ EXP(CG)*(ARF(K)+ARF(K+1))*DFR/6.28318
       CT=CT+AC*T11
       CTIME(J)=AC
                 WRITE (5,*)' CT  ',CT
 2000  ACCTM(J)=CT
       ELSE
C
C
      IF (FLAG .EQ. 3) THEN
      DO 210 K = 1,NFR
C                  ARF(K) = REF. DATA, CFR(K) = SAMPLE.
            ARF(K) = ARF(K) - CFR(K)
 210  CONTINUE
        ELSE IF (FLAG .EQ. 0) THEN
            DO 215 K = 1,NFR
                ARF(K) = CFR(K)
 215        CONTINUE
      END IF
      NFR1 = NFR - 1
      DFRTWO = DFR / TWO
      T11 = TIME / REAL(NTM -1)
C     TM(J) = TIME OF EACH PT. IN INV. DFT, USING TIME AS TOTAL
C     TIME OF SPECTRUM.
C
C           K = TIME  LOOP
C           J = FREQ. LOOP
C
      DO 220 K = 1,NTM
 220     TM(K) = REAL(K) * T11
      DFRTPI = DFR / TPI
      DO 250 K = 1,NTM
         AC   = QZERO
         DO 260 J = 1,NFR1
              T  = TM(K) * W(J)
              AT = CMPLX(ZERO,T)
              AC = AC + ARF(J) * EXP(AT)
 260     CONTINUE
         CSIMUL(K) = AC * DFRTPI
C                WRITE (5,*)' L  ARF   ',ARF(K)
         RACCUM(K) = REAL(RACCUM(K) + AC)
 250  CONTINUE
      END IF
      WRITE (4,*) TIME,',',T11,',',NTM
 400  FORMAT(1X,4(E12.6,','))
      WRITE(4,400) (RACCUM(J),J=1,NTM)
C
C       NOTE I2FLAG STILL IN.
C
      IF (I2FLAG .EQ. 5) THEN
          WRITE(7,400) (REAL(ACCTM(J)),J=1,NTM)
      ELSE
          WRITE(7,400) (REAL(CSIMUL(J)),J=1,NTM)
      END IF
      WRITE (5,*) 'DONE '
      WRITE (5,*) '        DONE '
      WRITE (5,*) '                DONE '
      WRITE (5,*) '                         DONE '
      WRITE (5,*) '                DONE '
      WRITE (5,*) '        DONE '
      WRITE (5,*) 'DONE '
      WRITE (5,*) 'DONE '
      WRITE (5,*) 'DONE '
      WRITE (5,*) 'DONE '
      WRITE (5,*) 'DONE '
      STOP
      END
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
```

```
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C                             SMOOTHING ROUTINE
C*********************************************************************
C*********************************************************************
      SUBROUTINE SMOOTH(NPR,DIF,ILOOP,L)
      REAL *4 TWO,QUART,R,HALF
      SAVE
      DIMENSION DIF(2048)
           TWO   = REAL(2.0)
           QUART = REAL(.25)
           HALF  = REAL(0.5)
      IST = NPR - 2
      L01 = L + 1
      L02 = L + 2
      NP1 = NPR - 1
           DO 90 K = 1 , ILOOP
                 A1=DIF(L)
                 A2=DIF(L01)
                 DQ=A1+ TWO *A2+DIF(L02)
                 DO 100 J = L01 , IST
                       J1 = J + 1
                       J2 = J + 2
                       DIF(J)  = QUART * DQ
                       DQ=DQ+DIF(J1)+DIF(J2)-A1-A2
                       A1=A2
                       A2=DIF(J1)
 100             CONTINUE
                 DIF(NP1) = QUART * DQ
                 DIF(NPR) = HALF * (A2 + DIF(NPR))
                 DIF(L)  = HALF * (DIF(L)  + DIF(L01))
 90         CONTINUE
           RETURN
           END
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C                         CALCULATE FREQ. IN Hz.
C*****************************************************************
C*****************************************************************
           SUBROUTINE PFREQ
           DIMENSION OHZ(2),OR(2)
           PI = 3.141592654
           OHZ(2) = 0.
           OR(2)  = 0.
           WRITE (5,*) 'NO OF FREQ. TO CONVERT, 1 OR 2  '
           READ(6,*) IJ
           OA = 2 * PI
           DO 210 I = 1 , IJ
           WRITE (5,*) 'FREQ. IN Hz    '
           READ(6,*) OHZ(I)
           OR(I) = OHZ(I) * OA/1E9
 210       CONTINUE
           WRITE (5,*) '   HZ(1)    R/nsec   HZ(2)   R/nsec '
           WRITE (5,*) OHZ(1),OR(1),OHZ(2),OR(2)
           RETURN
           END
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
      SUBROUTINE BEE(EINF,EPS,W,NP,NRLX,ARF,SD,REF,TAU,CFR)
      IMPLICIT COMPLEX (A-C)
C
      SAVE
      DIMENSION W(2048),ARF(2048)
      DIMENSION REF(2048),CFR(2048),EPS(5),TAU(5)
      DIMENSION UNREAL(2048),RACCUM(2048)
C
C          DIMENSION UNREAL(2048),RACCUM(2048),     CRAT(2048)
C
        WRITE (5,*) ' SET UP FREQ. DOMAIN MATRICES'
C
C     Set up freq. domain matrices of dielectric constants and the ratio of
C     R(jw)/V(jw).  The ratio is obtained by manipulating the eq. used to
C     for the dielectric in sample termination TDS.
```

```
C               E-1=(C/D) * ((V-R)/(j*w*(V+R))) * Z * COT(Z)
C               j=SQRT(-1)
C               IE    THE COMPLEX DIELECTRIC FUNCTION
C               Z=w*D/C*SQRT(E+1)
C               C     THE SPEED OF LIGHT
C               w=W   THE ANGULAR FREQ.
C               D     THE SAMPLE DEPTH
C
C     AEPS = E, OR AEPS = (E -1)
C     CZETA = Z
C     AZTA  = CMPLX(1.,0.), OR AZETA = Z / SIN(Z), OR AZETA = (c/d)*(Z)COT(Z)
C     ARF   = CFT OF REFERENCE DATA
C     CFR   = FREQ. DOMAIN DATA OF SAMPLE
C     CSDTHW= (w * d) / c
C
      DATA ZERO, ONE, TWO / 0., 1., 2./
      DATA THIRTY,QUART,TPI/30.,.25,6.2831853/
      CONE = CMPLX(ONE,ZERO)
      CTHSD  = CMPLX(THIRTY / SD,ZERO)
      SDTH  = SD / THIRTY
      DO 40 J=1,NP
C                 *** J. PHYS. CHEM. (1981) Vol. 85, p. 1065
           AEPS = CMPLX(EINF,ZERO)
           DO 43 K=1,NRLX
 43        AEPS = AEPS + CMPLX(EPS(K),ZERO)/(CMPLX(ONE,W(J) * TAU(K)))
           CSDTHW = CMPLX(W(J) * SDTH,ZERO)
           CZETA = CSDTHW * SQRT(AEPS + CONE)
C               CZETA = CSDTHW * SQRT(AEPS)
           AZTA = CONE
           IF (W(J) .EQ. ZERO) WRITE (5,*)' FREQ. = 0. AT PT ',J
           IF (W(J) .EQ. ZERO) GOTO 45
           AZTA = CZETA / SIN(CZETA)
 45        AZTA = CTHSD * AZTA * COS(CZETA)
           AI   = (AEPS - CONE)
           AY   = CMPLX(ZERO,W(J)) * AI
           CRAT = (AZTA-AY)/(AZTA+AY)
           CFR(J)  = CRAT * ARF(J)
C          REF(J) = REAL(CFR(J))
C          UNREAL(J) = AIMAG(CFR(J))
 40   CONTINUE
        RETURN
        END
```

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BIOGRAPHICAL SKETCH

Ernest Franklin Stine, Jr., was born January 20, 1957, in Raleigh, North Carolina.

Upon graduation from Rose High School (Greenville, N. C.) in 1975, he attended college at East Carolina University where (in the Spring of 1979) he received a B.S. degree (magna cum laude), with a major in chemistry and all necessary credits for a B.S. in biochemistry. From the Fall through the Summer of 1979, he worked as a research assistant at E.C.U. for Dr. Donald Clemens and Texas Gulf.

In August, 1979, the author entered the graduate program of the University of Florida (Gainesville, Florida). While there, he received the Chemistry Department Teaching Award. He studied the synthesis and photochemistry of tris 2,2'-Bipyridyl Ruthenium(II) Chloride and its analogs under Dr. Eric V. Dose and the electron transfer rate in mixed valence compounds under Dr. Russell S. Drago.

On December 23, 1979, he married another E.C.U. alumna, Portia Jean Carver.

In February, 1984, he joined the research staff of Dow Chemical in Baton Rouge, Louisiana.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Russell S. Drago, Chairman
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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Professor of Physics

This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December 1985

Dean, Graduate School